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DOE HANDBOOK

PRIMER ON SPONTANEOUS HEATING AND PYROPHORICITY

U.S. Department of Energy **FSC-6910**
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FOREWORD

The *Primer on Spontaneous Heating and Pyrophoricity* is approved for use by all DOE Components. It was developed to help Department of Energy (DOE) facility contractors prevent fires caused by spontaneous ignition. Spontaneously ignitable materials include those that ignite because of a slow buildup of heat (spontaneous heating) and those that ignite in air (pyrophoricity). The scientific principles of combustion and how they affect materials known to be spontaneously combustible are explained. The fire hazards of specific spontaneously heating and pyrophoric materials are discussed as well as techniques to prevent their ignition. Suitable fire extinguishing agents are included for most materials as well as safety precautions for storage and handling.

The DOE Primers are fundamental handbooks on safety-related topics of interest in the DOE Complex and are intended as an educational aid for operations and maintenance personnel and others who may have an interest in this topic. The Primers attempt to supply information in an easily understandable form which will help workers perform their duties in a safe and reliable manner. Persons trained in other technical areas may also find the Primers useful as a guide or as a reference source for further investigation.

Beneficial comments (recommendations, additions, deletions) and any pertinent data that may improve this document should be sent to:

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OVERVIEW

The *Department of Energy (DOE) Primer on Spontaneous Heating and Pyrophoricity* was prepared as an information resource for DOE and contractor personnel who may have these types of materials at their site. An understanding of spontaneous heating and pyrophoricity hazards is necessary for DOE facility personnel to operate and maintain facilities and facility support systems in a safe manner.

The *Primer on Spontaneous Heating and Pyrophoricity* contains an introduction and sections on the following topics:

- Principles of Combustion;
- Spontaneous Heating/Ignition of Hydrocarbons and Organics;
- Pyrophoric Gases and Liquids;
- Pyrophoric Nonmetallic Solids;
- Combustible and Pyrophoric Metals; and
- Accident Case Studies.

The information contained in this Primer is by no means all encompassing. However, enough information is presented to provide the reader with a fundamental knowledge level sufficient to recognize most spontaneous ignition hazards and how to prevent ignition and widespread fires. Additional resource materials for this topic are listed in the bibliography section at the end of this Handbook.

INTRODUCTION

Some materials, such as phosphorus, ignite spontaneously when exposed to air. Other materials, such as coal, may take several weeks to ignite under similar conditions. This ignition time difference is the defining point between pyrophoricity and spontaneous heating. It is well known that fires caused by these phenomena do occur, sometimes resulting in personal injury and significant damage to facilities. By its very nature, spontaneous heating and pyrophoricity are among the most insidious types of fire hazards because here is usually no outward evidence of the potential for fire. Therefore, an understanding of the principles of spontaneous heating and pyrophoricity is necessary for instituting appropriate fire prevention measures. This Primer introduces DOE operations and maintenance personnel with basic information necessary to identify and prevent spontaneous ignition hazards.

Upon completion of this Handbook, the reader should be able to:

- Identify the four required elements of the Fire Tetrahedron necessary to support combustion.
- Define the following terms: combustion, oxidation, spontaneous heating, pyrophoricity, hypergolic, and specific area.
- Describe the effects that atmospheric oxygen, moisture, heat transfer, and specific area have on spontaneous heating and ignition.
- Identify five metals and three gases known to be pyrophoric.
- Identify acceptable methods for long-term storage of spontaneously heating and pyrophoric materials.
- Identify the appropriate measures for preventing fires caused by spontaneous heating and pyrophoricity.
- Identify references for obtaining further information on oxidizers, pyrophoric materials, hypergolic substances, and fire extinguishing agents.
- Identify proper emergency response, including extinguishing agents for various spontaneously igniting materials, and self-extinguishing without interaction.
- Describe the importance of good housekeeping in limiting fire damage.

DEFINITIONS

Combustion:	A chemical process of oxidation that occurs at a rate fast enough to produce heat and usually light in the form of either a glow or flame.
Hypergolic	Any substance that will spontaneously ignite or explode upon exposure to an oxidizer.
Ignition Temperature:	Minimum temperature a substance should attain in order to ignite under specific test conditions.
Oxidization:	A reaction driven by the removal or transfer of electrons between atoms or molecules.
Oxidizer:	Any solid or liquid that readily yields oxygen or other oxidizing gas; or that readily reacts to promote or initiate combustion of combustible materials. Additionally an oxidizer, under certain circumstances, can undergo a vigorous self-sustained decomposition due to contamination or heat exposure.[1]
Oxidizing Agent:	Any material that readily yields oxygen or other oxidizing gas; or that reacts chemically to oxidize combustible materials.
Pyrolysis	A process in which material is decomposed into simpler molecular compounds by the effects of heat alone; pyrolysis often precedes combustion.
Pyrophoric	A chemical property characterized by the ability of a material to undergo a spontaneous ignition in air. A material that, even in small quantities and without an external ignition source, can ignite at or below 54.4°C (130°F) in contact with air.
Specific Area:	Amount of surface area per unit weight of a material, usually expressed in cm^2/g (in^2/lb).
Specific Surface Area:	The ratio of reactive surface area to the mass of the material (typically a factor of 3-5 times higher than the Specific Area previously defined).
Spontaneous Heating:	Process whereby a material's temperature increases due to its exothermic reaction with oxidants without drawing heat from its surroundings.

[1] See NFPA 400-2013, *Hazardous Materials Code* for more information on Oxidizer classifications, including a list of the most common oxidizers.

PRINCIPLES OF COMBUSTION

Combustion

NFPA defines combustion as a chemical process of oxidation that occurs at a rate fast enough to produce heat and usually light in the form of either a glow or flame.

Many materials oxidize to some degree; however, the rates of oxidation differ between materials. The difference between slow and rapid oxidation is that the latter occurs so rapidly that heat is generated faster than it is dissipated, causing the material (fuel) being oxidized to reach its ignition temperature. Once the ignition temperature is reached, the material will continue to burn until the fuel or oxygen is consumed. A visible flame usually accompanies the heat release during combustion. However, some materials, such as charcoal, smolder rather than produce a flame. Other materials, such as uranium and plutonium, can burn without a visible flame.

A familiar slowly occurring oxidation reaction is the rusting of iron. Such a reaction releases heat so slowly that the temperature hardly increases more than a few degrees above ambient temperature. These slow reactions do not cause fires and are not considered combustion.

The Fire Tetrahedron

Generally, there are four items necessary to support combustion:

1. Oxidizing Agent;
2. Fuel;
3. Heat Source; and
4. Uninhibited Chain Reaction.

These are depicted pictorially in Figure 1, which is commonly called the Fire Tetrahedron. This graphic shows that for combustion to occur, fuel, an oxidizing agent, a heat source and an uninhibited chain reaction all need to be present in the same place at the same time. If any one of the legs of the tetrahedron is removed, the fire will be extinguished.

Oxidizing Agent

An oxidizing agent (or oxidizer) is a material that readily yields oxygen or other oxidizing gas - or that reacts chemically to oxidize combustible materials. By far the most common oxidizing agent is the oxygen in the earth's atmosphere; however, there are many chemical compounds that also act as oxidizing agents. Some of these agents react with fuels more readily and violently than oxygen. Further information on the relative hazards and classifications of oxidizing agents may be found in Appendix G in NFPA 400, *Hazardous Materials Code*.

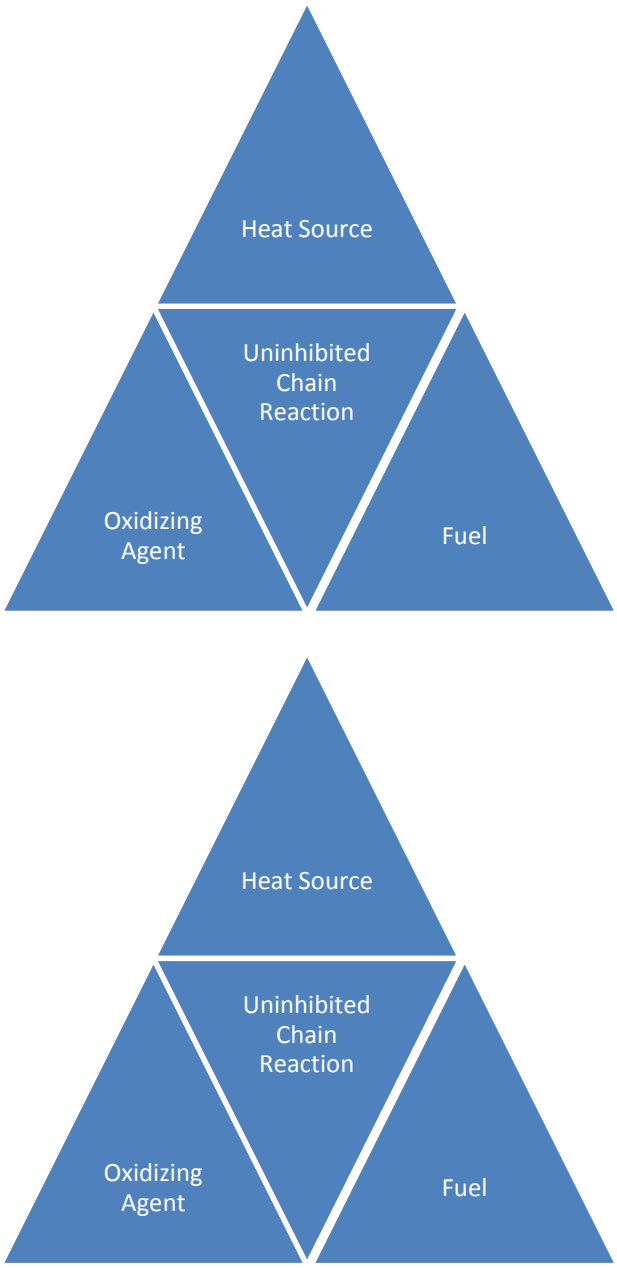

Figure 1. Fire Tetrahedron

Fuel

A fuel is the substance that reacts with the oxidizing agent during combustion. Fuels can be solids, liquids, gases, and even metals. Familiar fuels are coal, firewood, and gasoline. For the purpose of this document, the discussion of fuels will be limited to those that are known to combust spontaneously or that involve metals.

Heat Source

Normally, a heat source such as a flame or spark is required to ignite a mixture of a fuel and oxidizing agent (heat needs to be added or the fuel and oxidizing agent will not react). But sometimes the heat source may not always be external. The reactions that are the subject of this document are special instances where no external heat source is required to ignite the fuel. These fuels react so readily with an oxidizer that an external heat source is not required for ignition due to the highly exothermic nature of the reaction. Ignition for these fuels therefore occurs spontaneously.

Uninhibited Chain Reaction

Once the fire is started, this exothermic reaction feeds heat back to the fuel to produce the gaseous fuel used in the flame. In other words, the chain reaction can provide the heat necessary to maintain the fire.

Spontaneous Ignition

Spontaneous ignition is the ignition of a fuel caused by the accumulation of heat from either a hypergolic reaction or pyrophoric reaction.

Hypergolic and Pyrophoric Reactions

A hypergolic reaction describes a material's ability to immediately ignite or explode upon contact with an oxidizing agent (e.g., rocket fuel mixture – simply combining hydrazine (fuel) with nitrogen tetroxide (oxidizing agent) will cause spontaneous ignition with or without the presence of oxygen). Pyrophoricity is a special case of a hypergolic reaction where a substance spontaneously ignites upon exposure to air (atmospheric oxygen). A pyrophoric material may be a solid, liquid, or gas. Pyrophoric materials are not compatible with air, moisture, oxygen/oxidizer, and protic solvents including water, acids, alcohols, amines, mercaptans, etc. Although there are some pyrophoric liquids and gases, most pyrophoric materials prudent to safety practices are metals that will react rapidly under the condition of having a large specific surface area. In practice, increasing the material mass and/or decreasing its surface area will decrease the material specific surface area that will suppress its pyrophoric characteristics.

The remainder of this document will be concerned only with spontaneous heating and pyrophoricity.

Spontaneous Heating

Spontaneous heating is a phenomenon caused by an unstable (usually oxidizable) material and its decomposition compounds with exothermic reactions releasing heat. The retention of the generated heat in the material by virtue of its poor thermal heat loss (i.e., conduction, convection or radiation) will cause the temperature of the material to rise. Under some circumstances, this process can lead to flaming combustion and overt fire, in which case it is properly called spontaneous ignition, and is regarded as a special case of spontaneous combustion.

Spontaneous heating can be the result of direct oxidation of hydrocarbons (for example, oils, coal, and solvents) or it may occur because of the action of microorganisms in organic materials (not included within the scope of this text). A more detailed discussion on spontaneous heating is included in the next section.

SPONTANEOUS HEATING/IGNITION OF HYDROCARBONS AND ORGANICS

Spontaneous Heating/Ignition of Hydrocarbons

Some hydrocarbons are capable of spontaneous heating and ignition under proper conditions. This phenomenon usually involves a liquid hydrocarbon in contact with combustible materials. Likewise some solid hydrocarbons, such as coal, can react directly with atmospheric oxygen to create a condition for combustion. Whether spontaneous heating leads to ignition or not depends on several factors including:

- The critical stacking temperature which is influenced by rate at which heat is generated and removed from the stacking material.
- The critical ambient temperature of the combustible material (e.g., fibrous, particle, dust, shaving, chips, even large pieces), hydrocarbon, or any thermally generated gaseous products.
- The specific area of the hydrocarbons exposed to the oxidizer.
- The mass of the material being oxidized.

For spontaneous ignition to occur, the rate of heat being generated by the chemical reaction needs to exceed the rate of heat removal by conduction, convection, and radiation (thermal). As the temperature of the material begins to rise, the rate of heat generation will often increase. The result is a "runaway" reaction, which ultimately causes ignition. If the rate of heat removal equals the rate of generation however, the material will not increase in temperature and ignition will not occur.

When a volume of material is undergoing a chemical reaction, the material located near the surface of the pile may be able to release adequate heat away from the material to prevent combustion. However, the sub-surface materials are somewhat insulated and can't release heat at an adequate rate so the inner core of the material heats to the auto-ignition temperature of the material being oxidized which results in combustion.

The rate of heat removal may be increased through physical contact with a thermally conductive surface, by rotating piles of combustibles to cool hot spots, spreading out the material to create a thin layer, and by circulating inert gases through the piles to cool hot spots and displace the oxidizing agent.

These principles are illustrated in Figure 2. Although coal is used as the example, the principles depicted apply to all materials which are known to heat spontaneously (including pyrophoric liquids, gasses (unoxidized) metals and other solids).

The ignition temperature of the material is obviously of concern and varies widely among materials. Much more stringent controls should be placed on materials which have lower ignition temperatures and those which liberate explosive gases. Although most materials with high ignition temperatures are of lesser concern, some are more explosive than those with lower ignition temperatures. Safety Data Sheets (SDSs) are a source for information such as ignition temperature, vapor pressure, toxicity, and reactivity.

The specific area of a combustible substance is a ratio of the surface area of the material exposed to an oxidizing atmosphere to the mass. Materials that have a high specific area are more prone to heat generation and spontaneous ignition. Flammable or combustible liquids on fibrous materials pose an

increased spontaneous ignition fire hazard (i.e. oils soaked into rags or paintbrushes, absorbent pads in an oil catch pan). The fibers of the material allow the liquid to spread out over a larger surface area, allowing more contact with oxygen. Therefore, the thinly layered combustible liquids spread over fibrous materials are easily oxidized. The process of oxidation generates heat and an exothermic reaction can occur.

As the ambient temperature rises, the rate of spontaneous heat generation will also rise. High ambient temperatures also reduce the rate of heat removal, bringing the hydrocarbon closer to its ignition temperature.

With these facts in mind, the following housekeeping steps will help minimize the threat of spontaneous heating and ignition of hydrocarbon or organic compounds:

- Keep potentially spontaneously heating materials in a cool environment. The heat transfer resulting from a cooler atmosphere or circulating air will lower the temperature of the materials.
- Know all of the chemicals in your inventory and their potential self-heating hazards along with their ignition temperatures. Consult the chemical manufacturer's SDSs and subject matter experts where available.
- Reduce the amount of fibrous materials (e.g., rags) used with combustible liquid hydrocarbons.
- Enact passivation techniques such as spreading the material out in a thin layer over a large surface area or slowly allowing the material to oxidize in a controlled environment. This increases the dissipation of heat caused by oxidation. If the materials cannot be spread out, consider storing the materials in an approved waste receptacle designed to contain any potential fire.
- Keep appropriate fire extinguishing equipment near potential areas of ignition. Type A extinguishing agents are appropriate for most nonhazardous, combustible materials (rags, wood, textiles), whereas a Type B agent is necessary in the presence of quantities of combustible liquids. Class D extinguishing agents for metal fires are discussed in a later section and require specific agents for particular materials.
- Fire hazard planning is important for both fire prevention and fire protection activities. It may be more appropriate to control or allow a fire to self-extinguish rather than trying to attempt extinguishment manually or automatically. For example, attempting to extinguish a fire within a processing area may have the potential to contaminate the processing line while allowing the small quantity of material to continue to burn would result in minor damage if other materials are not involved.
- Keep combustible materials away from known materials with spontaneous heating hazards. Many fires have been started as the result of a self-heating material being exposed to a combustible with a low ignition temperature. This practice is also important from a fire loss minimization aspect.
- Place combustible metals on substantial metal surfaces that can act as a heat sink.

Spontaneous ignition may occur in piles of moist organic material where heat is generated in the early stages by the respiration of bacteria, molds, and microorganisms. High moisture content is required for vigorous activity, and heating is generally controlled by maintaining the moisture content below a

predetermined level. This type of heating can only raise the material to the temperature range of 50 to 75°C (122 to 167°F), where the living organisms die. Beyond this point, other oxidation reactions must take over if ignition is to occur. The existence of biological heating requires careful control of moisture, air supply, and nearby combustible or flammable materials. Heat generated by biological action may also act as a catalyst for other reactions that occur only at elevated temperatures. In addition, if a "hot spot" in a pile of organic material is exposed to a highly flammable liquid or gas, a fire or explosion may occur.

The likelihood of biological heating may be reduced by the following measures:

- Provide adequate ventilation of the organic material to remove moisture, heat, and dust particles.
- Limit the storage time of the organic material using a "first in, first out" rule of thumb.
- Circulate large quantities of organic materials to disperse areas bof localized heating.

Appendix A lists many organic materials known to heat spontaneously and measures to prevent their ignition.

Spontaneous Oxidation and Heating of Coal

Coal presents hazards between the time it is mined and its eventual consumption in boilers and furnaces. Below are listed some of the characteristics of spontaneous fires in coal. These characteristics can be used to evaluate the potential for coal fires and as guidelines for minimizing the probability of a fire:

1. The higher the inherent (equilibrium) moisture, the higher the heating tendency.
2. The lower the ash free Btu, the higher the heating tendency.
3. The higher the oxygen content in the coal, the higher the heating tendency.
4. Sulfur is a factor in the spontaneous heating of coal, but the exact extent is unknown. There are many very low-sulfur western subbituminous and lignite coals that have very high oxidizing characteristics and there are high sulfur coals that exhibit relatively low oxidizing characteristics.
5. The oxidation of coal is a solid/gas reaction, which happens initially when air (a gas) passes over a coal surface (a solid). Oxygen from the air combines with the coal, raising the temperature of the coal. As the reaction proceeds, the moisture in the coal is liberated as a vapor and then some of the volatile matter that normally has a distinct odor is released. The amount of surface area of the coal that is exposed is a direct factor in its heating tendency. The finer the size of the coal, the more surface is exposed per unit volume and the greater the oxidization rate (See Figure 2).
6. Many times, segregation of the coal particle sizes is the major cause of heating. The coarse sizes allow the air to enter the pile at one location and react with the high surface area fines at another location. Coals with a large top size [e.g., 100 mm ($\geq$4 in.)], will segregate more in handling than those of smaller size [50 mm ($\geq$2 in.)].
7. It is generally believed that the rate of reaction doubles for every 8 to 11°C (15 to 20°F) increase in temperature.

8. Freshly mined coal has the greatest oxidizing characteristic, but a hot spot in a pile may not appear for one or two months. As the initial oxidization takes place, the temperature gradually increases and the rate of oxidization accelerates.
9. There is a critical amount of airflow through a portion of a coal pile that maximizes the oxidation or heating tendencies of coal. If there is no airflow through a pile, then there is a limited supply of oxygen to keep up with oxidation that can lead to ignition. If there is a plentiful supply of air, any heat generated from oxidation will be carried off and the pile temperature will reach equilibrium with the air temperature; this is considered a ventilated pile. When there is just sufficient airflow for the coal to absorb most of the oxygen from the air and an insufficient airflow to dissipate the heat generated, the reaction rate increases and the temperatures may eventually exceed acceptable limits.

Coal Storage

Coal should be stored in properly designed bunkers, silos, bins, or in outside piles. The most important aspects of coal storage are minimizing the flow of air through the pile, using the "first-in, first out" rule of thumb, and minimizing the amount of finely divided coal in the pile. “Hot spots" should be removed or exposed to the atmosphere to allow cooling. Coal should be compacted to minimize the amount of air in the pile.

Caution should be used when determining if water will be applied to a hot spot. The size and location of the hot spot are significant variables that need to be considered. The application of water to large, sub-surface hot spots may result in a steam explosion.

Outside coal piles should not be located over pressurized utility lines (water, gas, etc.).

Coal that is stored in bunkers has a limited amount of time prior to the formation of hot spots. Depending on the design and capacity of a specific bunker, coal should be rotated through the bunker on a periodic basis. When maintenance activities occur that prevent the rotation of the coal through the bunker, consideration should be given to completely emptying the bunker prior to performing the maintenance activity.

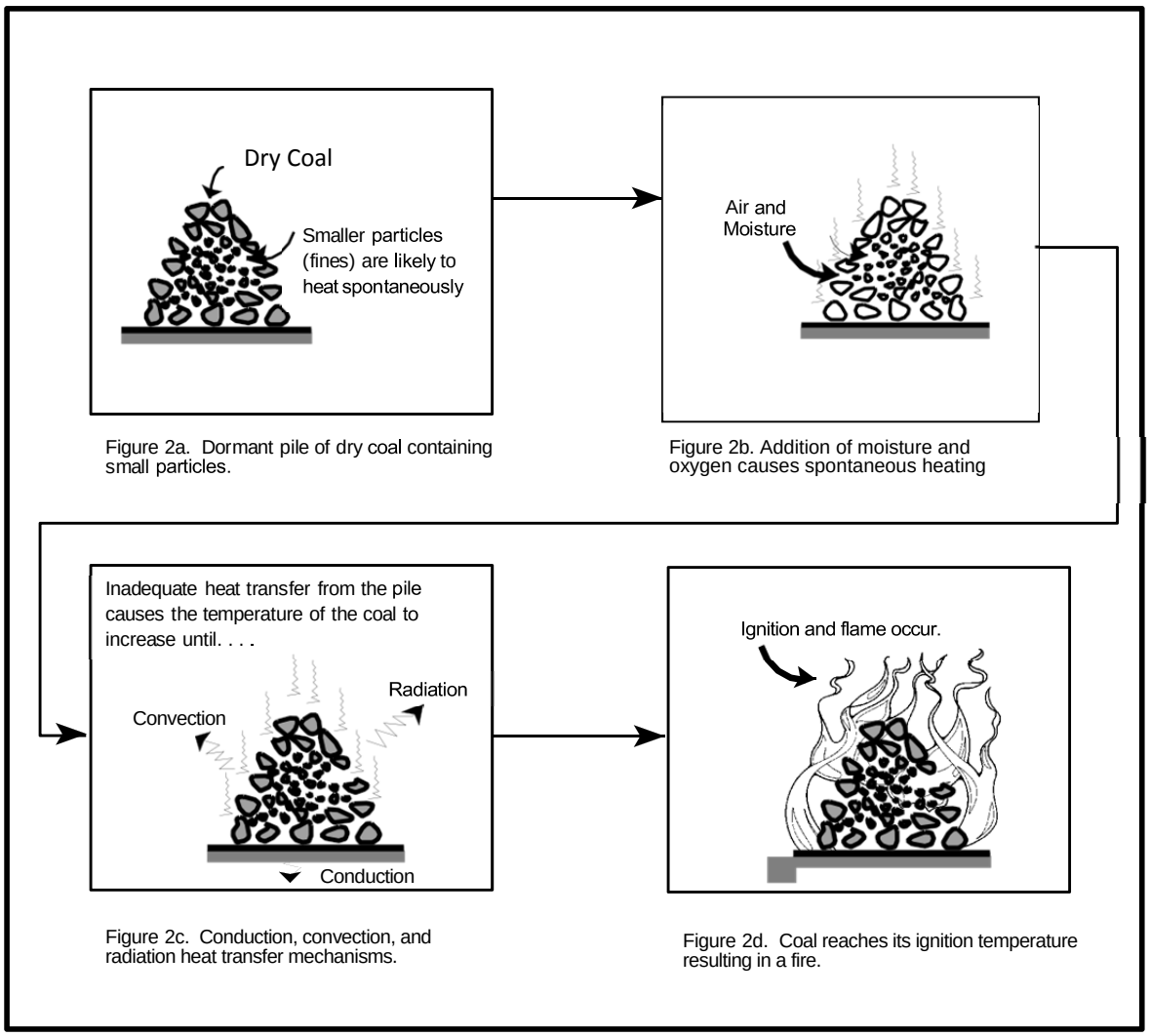

Figure 2a. Dormant pile of dry coal containing small particles.

Figure 2b. Addition of moisture and oxygen causes spontaneous heating

Figure 2c. Conduction, convection, and radiation heat transfer mechanisms.

Figure 2d. Coal reaches its ignition temperature resulting in a fire.

Figure 2. The evolution of a coal fire caused by spontaneous heating.

PYROPHORIC GASES AND LIQUIDS

Pyrophoric Gases

There are several pyrophoric gases that should be included in any discussion of pyrophoricity. Many of these are used in manufacturing of microelectronics. All of the gases presented here have three things in common: 1) they may ignite immediately upon exposure to air at certain temperatures; 2) they are all nonmetallic hydrides; and 3) many other compounds that contain these gases in their molecular structure are also pyrophoric.

Arsine

Arsine (AsH_3), also known as arsenic hydride, is a colorless, flammable, pyrophoric, and highly toxic gas that is one of the simplest compounds of arsenic with a distinctive garlic-like odor. It is heavier than air and is a blood and nerve poison. Arsine will generally not ignite in air unless it is at an elevated temperature, but it can explode with a suitably powerful initiator (heat source, shock wave, electrostatic discharge). Arsine may also exist in other compounds. The ignition temperatures of many of these arsine containing compounds are lower than that of arsine, causing them to ignite in air even at low temperatures (below 0°C, 32°F). All arsine compounds should be considered pyrophoric until they are properly characterized and determined not to be pyrophoric. Do not use water to extinguish fires involving arsenic compounds (e.g. arsenic trichloride); dry chemical or carbon dioxide extinguishers should be used; the use of water should be avoided because of the possibility of highly toxic run-off from the site. Fire service personnel should be advised that self-contained breathing apparatus and totally encapsulated protective clothing are necessary.

Diborane

Diborane (B_2H_6) is a highly toxic, colorless gas with a repulsive but sweet odor; it is highly reactive and flammable. It forms flammable mixtures with air over a wide range (flammable limits, 0.9% and 98%). The ignition temperature of diborane is between 38°C and 52°C (100°F and 125°F). Diborane will ignite spontaneously in moist air at room temperature. It reacts spontaneously with chlorine and forms hydrides with aluminum and lithium, which may ignite spontaneously in air. It reacts with many oxidized surfaces as a strong reducing agent, and reacts violently with vaporizing liquid-type extinguishing agents.

Storage should be in a detached, refrigerated (less than 20°C, 68°F), and well- ventilated place. Boranes should be separated from halogens and other oxidizing agents and checked periodically for decomposition. Protect against electrical spark, open flames, or any other heat source. A dry nitrogen purge should be used in any transfer. Waste material should be completely hydrolyzed with water before disposal. Combustible solutions should be burned as a means of disposal. There are no special shipping requirements for diborane other than steel pressure cylinders.

Firefighting should be done from an explosion-resistant location. Use water from unmanned monitors or hose holders to keep fire-exposed containers cool. If it is necessary to stop the flow of gas, use water spray to protect personnel effecting shut-off. Halon should not be used as an extinguishing agent on diborane fires.

Phosphine

Phosphine (PH_3) is a colorless, flammable and highly toxic, gas with a fishy or garlic-like odor. This chemical is very dangerous, with an ignition temperature of 100°C (212°F), often igniting spontaneously. Phosphine gas readily combines with nitrates, halogens, and metals to form very explosive and volatile compounds. Specifically, phosphine reacts violently with air, boron trichloride, (BCl_3), bromine (Br_2), chlorine (Cl_2),hypochlorite (ClO), Mercury(II) nitrate ($Hg(NO_3)_2$), nitric oxide (NO), nitrous oxide (N_2O), nitrogen trichloride (NCl_3), nitrate (NO_3), Nitrous acid (HNO_2), oxygen gas (O_2), potassium in anhydrous ammonia ($K+NH_3$), and silver nitrate ($AgNO_3$).

At elevated temperatures, phosphine decomposes, emitting highly toxic fumes of PO_x, which react vigorously with oxidizing materials. It possesses the characteristic putrefying odor of a mixture of garlic and decaying fish. Prolonged exposure to very low concentrations will cause chronic poisoning, characterized by anemia, bronchitis, gastro-intestinal disturbances, and visual, speech, and motor difficulties.

Silane

Silane (SiH_4), also known as silicon tetrahydride, is a colorless gas with a putrid odor. It and its compounds (e.g., disilane Si_2H_8) can ignite in air and react violently with chlorine (Cl_2). The presence of other hydrides as impurities causes ignition always to occur in air. However, 99.95% pure silane ignites in air unless emerging at very high gas velocities, whereas mixtures of up to 10% silane may not ignite. Hydrogen liberated from its reaction with air (atmospheric oxygen) often ignites explosively. Silanes react violently with chlorine and bromine. All silanes should be considered pyrophoric until they are properly characterized. Halon should not be used as an extinguishing agent on silane fires. For additional information on the safe handling of silane see: AIGA 052/08, *Storage and Handling of Silane and Silane Mixtures*.

Extinguishing Pyrophoric Gas Fires

Pyrophoric gases may spontaneously explode at high gas release rates. For fires involving flammable gases, the best procedure is to stop the flow of the gas before attempting extinguishment of the fire. To extinguish the fire while allowing continued flow of the gas is extremely dangerous; an explosive cloud of gas/air mixture may be created that, if ignited, may cause far more damage than the original fire. Extinguishing the flame using carbon dioxide or dry chemical may be desirable to allow immediate access to valves to shut off the flow of gas, but this needs to be done carefully. In many cases, it will be preferable to allow continued burning, while protecting exposures with water spray, until the flow of gas can be stopped. Since many pyrophoric gases react violently with halogens, Halons should not be used as extinguishing agents.

Pyrophoric Gas Storage and Dispensing Areas

Pyrophoric gas cylinders in storage or dispensing areas should be provided with safeguards as described in NFPA 318,*Standard for the Protection of Semiconductor Fabrication Facilities*; NFPA 55, *Compressed Gases and Cryogenic Fluids Code*; and, the *International Building Code*. Additionally, NFPA 70, *National Electrical Code*, should be consulted for hazard classification and protection techniques of electrical equipment near

flammable gas storage areas. It should also be noted that pyrophoric gases are not allowed to be used or stored in an unsprinklered building.

Pyrophoric Nonmetallic Liquids

Hydrazine

Properties

Hydrazine is a colorless oily liquid resembling water in appearance and possesses a weak, ammonia-like odor. Its chemical formula is N_2H_4. Commercially it is available as an anhydrous (without water) liquid and in aqueous solutions. Hydrazine is most well-known for its use as a rocket fuel, but is also used in manufacturing agricultural chemicals, explosives, and plastics. It fumes in air and reacts with all oxidizing agents. Hydrazine is *hypergolic*, meaning that it reacts explosively upon contact with many oxidizing agents. The flash point of hydrazine is 38° C (100°F). Its ignition temperature is 270°C (518°F) on a glass surface but may be as low as 23°C (74°F) when in contact with a strong oxidizing agent. Hydrazine forms flammable mixtures with air from 4% to 100% by volume and decomposes when heated. Hydrazine ignites in air at room temperature when exposed to metal oxide surfaces and in a wide variety of porous materials.

Storage and Handling

Storage in a detached building is preferred. Inside storage should be in a standard flammable liquids storage warehouse, room, or cabinet. An emergency water supply and automatic sprinklers are also necessary for fire extinguishment. Hydrazine should be stored separately from metal oxides, acids, and all oxidizing agents. Hydrazine is highly toxic and may be fatal if inhaled or absorbed through the skin. It is also corrosive and may cause severe eye and skin burns. Protective clothing that prevents penetration of hydrazine and positive pressure self-contained breathing apparatus are advisable when working with hydrazine.

Extinguishing Hydrazine Fires

Fires involving hydrazine may produce irritants and toxic gases such as nitrogen oxides. Fires should not be approached without protective clothing and positive pressure respirators. Hydrazine fires should be approached from upwind to avoid hazardous vapors and toxic decomposition products. Flooding amounts of water should be applied as a fog or spray. Water should be sprayed on fire-exposed containers of hydrazine to keep them cool. Fires should be fought from a protected location or at a maximum possible distance. Flooding amounts of water may be necessary to prevent reignition.

PYROPHORIC NONMETALLIC SOLIDS

Phosphorus

There are three different allotropes of phosphorus (P_4). These are commonly known as white, yellow, and red phosphorous. Red phosphorus is not considered pyrophoric. However, red phosphorus ignites easily and produces phosphine (a pyrophoric gas) during combustion.

Pyrophoric white phosphorus is a colorless to yellow, translucent, nonmetallic solid. It ignites spontaneously on contact with air at or above 30°C (86°F). Phosphorous is explosive when mixed with oxidizing agents. Fumes from burning phosphorus are highly irritating but only slightly toxic except in very high concentrations. Like red phosphorus, white phosphorus also produces phosphine during combustion.

When storing, protect containers against physical damage. Phosphorus should always be kept underwater, or under an inert atmosphere, separated from oxidizing agents and combustible materials. When shipping, keep phosphorus under water in hermetically sealed cans inside wooden boxes, under water in drums, or in tank motor vehicles or tank cars under water or blanketed with an inert gas. Refer to NFPA 484, *Combustible Metals*, 2015, for additional information on sprinkler protection guidance.

Phosphorous fires should be deluged with water until the fire is extinguished and the phosphorus has solidified. The solidified phosphorus should then be covered with wet sand, clay, or ground limestone.

COMBUSTIBLE AND PYROPHORIC METALS

This section covers the pyrophoricity of combustible metals. Properties of various combustible metals are discussed as well as the conditions in which they become pyrophoric. For additional information on the fire hazards of combustible and pyrophoric metals, see Chapter 14 of the Ignition Handbook.

Nearly all metals will burn in air under certain conditions. Some are oxidized rapidly in the presence of air or moisture, generating sufficient heat to reach their ignition temperatures. Others oxidize so slowly that heat generated during oxidation is dissipated before the metal becomes hot enough to ignite. Certain metals, notably magnesium, titanium, sodium, potassium, lithium, zirconium, hafnium, calcium, zinc, plutonium, uranium, and thorium, are referred to as combustible metals because of the ease of ignition when they reach a high specific surface area (thin sections, fine particles, or molten states). However, the same metals in heavier pieces, such as ingots and thick wall castings (not thin sections or fine particles or molten states) are comparatively difficult to ignite.

Some metals, such as iron and steel, which are not normally thought of as combustible, may ignite and burn when in finely divided form (powders and dusts). Generally, iron and steel are not considered pyrophoric but may be in certain particle ranges and under very specific conditions. For example, clean, fine steel wool may be ignited. Particle size, shape, quantity, and alloy are important factors to be considered when evaluating metal combustibility. Combustibility of metallic alloys may differ and vary widely from the combustibility characteristics of the alloys' constituent elements. Metals tend to be most reactive when in finely divided form, and some may require shipment and storage using an inert gas or liquid to reduce fire risks. Combustible dusts dispersed in air can present a dust explosion hazard and appropriate controls need to be implemented to prevent aerosolizing or dispersing combustible dust; for additional information, please see

NFPA 654, 2013, *Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids.*

Hot or burning metals may react violently upon contact with other materials, such as oxidizing agents and extinguishing agents used on fires involving ordinary combustibles or flammable liquids. Temperatures produced by burning metals can be higher than temperatures generated by burning flammable liquids. Some metals can continue to burn in carbon dioxide, nitrogen, water, or steam atmospheres in which ordinary combustibles or flammable liquids would be incapable of burning.

Properties of burning metal fires cover a wide range. Burning titanium produces little smoke, while burning lithium produces a smoke that is dense and profuse. Some water-moistened metal powders, such as zirconium, burn with near explosive violence, while the same powder wet with oil burns quiescently. Sodium melts and flows while burning; calcium does not. Some metals (e.g., uranium) acquire an increased tendency to burn after prolonged exposure to moist air, while prolonged exposure to dry air makes it more difficult to ignite.

Water should never be applied to burning metals since the water can break down into its molecular structure (hydrogen and oxygen) which could result in a significantly increased fire and possibly a violent reaction. If a combustible metal is also in the presence of a flammable or combustible liquid, both the Class B and Class D fires must be considered, typically by extinguishing the metal fire first and then the liquid fire to avoid re-ignition.

The toxicity of certain metals is also an important factor in fire suppression. Some metals (especially heavy metals) can be toxic or fatal if they enter the bloodstream or their smoke fumes are inhaled. Metal fires should never be approached without proper protective equipment (clothing and respirators).

A few metals, such as thorium, uranium, and plutonium, emit ionizing radiation that can complicate firefighting and introduce a radioactive contamination problem. Where possible, radioactive materials should not be processed or stored with other pyrophoric materials because of the likelihood of widespread radioactive contamination during a fire. Where such combinations are essential to operations, appropriate engineering controls and emergency procedures should be in place to prevent fires or quickly suppress fires in the event the controls fail.

Because extinguishing fires in combustible metals involves techniques not commonly encountered in conventional firefighting operations, it is necessary for those responsible for controlling combustible metal fires to be thoroughly trained prior to an actual fire emergency. Refer to Combustible Metal Extinguishing Agents and Application Techniques on page 32 for information on extinguishing agents; refer to NFPA 484, *Combustible Metals*, 2015, for sprinkler protection guidance.

The following material discusses the properties of various combustible metals, conditions in which they become pyrophoric, storage and handling practices, processing hazards, and methods of extinguishing fires involving these kinds of metals. For more detailed information regarding fire reactive metals, please see NFPA 484 as well as Factory Mutual Datasheet 7-85 (April 2013) *Metals and Alloys*.

Magnesium

Properties

The ignition temperature of pieces of magnesium is very close to its melting point of 650°C (1,200°F) (See Appendix B). However, ignition of magnesium in certain forms may occur at temperatures well below 650°C (1,200°F). For example, magnesium ribbons and shavings can be ignited under certain conditions at about 510°C (950°F), and finely divided magnesium powder can ignite below 482°C (900°F).

Metal marketed under different trade names and commonly referred to as magnesium may be one of a large number of different alloys containing magnesium, but also significant percentages of aluminum, manganese, and zinc. Some of these alloys have ignition temperatures considerably lower than pure magnesium, and certain magnesium alloys will ignite at temperatures as low as 427°C (800°F). Flame temperatures of magnesium and magnesium alloys can reach 1,371°C (2,500°F), although flame height above the burning metal is usually less than 305 mm (12 in).

As is the case with all combustible metals, the ease of ignition of magnesium depends upon its size and shape. As noted earlier, the specific area of a combustible substance is the surface area of the substance exposed to an oxidizing atmosphere per gram of the substance and is usually expressed in cm^2/g. A combustible substance that has a high specific area is more prone to oxidize, heat, and ignite spontaneously. A match flame may ignite thin, small pieces, such as ribbons, chips, and shavings, whereas castings and other large pieces are difficult to ignite even with a torch because of the high thermal conductivity of the metal. In order to ignite a large piece of magnesium, it is usually necessary to raise the entire piece to the ignition temperature.

Scrap magnesium chips or other fines (finely divided particles) may burn as the result of ignition of waste rags or other contaminants. Chips wet with water, water-soluble oils, and oils containing more than 0.2% fatty acid may generate hydrogen gas. Chips wet with animal or vegetable oils may burn if the oils ignite spontaneously. Fines from grinding operations generate hydrogen when submerged in water, but they cannot be ignited in this condition. Containers used with fines should be provided with ventilation holes to allow for the dissipation of hydrogen gas. Grinding fines that are slightly wetted with water may generate sufficient heat to ignite spontaneously in air, burning violently as oxygen is extracted from the water with the release of hydrogen.

Storage and Handling

The larger a piece of magnesium, the more difficult it is to ignite, but once ignited, magnesium burns intensely and is difficult to extinguish. The storage recommendations in NFPA 484 take these properties into consideration. Recommended maximum quantities of various sizes and forms to be stored in specific locations are covered in this standard. Storage buildings should be noncombustible, and the magnesium should be segregated from combustible material as a fire prevention measure.

With easily ignited lightweight castings, segregation from combustible materials is especially important. In the case of dry fines (fine magnesium scrap), storage in noncombustible covered containers in separate fire resistive storage buildings or rooms with explosion venting facilities is preferable. The use of sprinklers in

magnesium scrap storage buildings or area is prohibited. However, in some facilities magnesium is contained inside a robust steel container (e.g., Mag-Beds) with the container providing sufficient separation/confinement of the material that sprinklers will not be an issue. For combustible buildings or buildings containing combustible contents, or where combustibles are located within 9.14 m (30 ft) of the magnesium, NFPA 484 recommends automatic sprinkler protection to assure prompt control of a fire before the magnesium becomes involved.

Because of the possibility of hydrogen generation and of spontaneous heating of fines wet with coolants (other than neutral mineral oil), it is preferable to store wet scrap fines outdoors. Covered noncombustible containers should be vented to allow for the dissipation of hydrogen gas.

Process Hazards

In machining operations involving magnesium alloys, sufficient frictional heat to ignite the chips or shavings may be created if the tools are dull or deformed. If cutting fluids are used (machining of magnesium is normally performed dry), they should be of the mineral-oil type that have a high flash point. Water or water-oil emulsions are hazardous, since wet magnesium shavings and dust liberate hydrogen gas and burn more violently than dry material when ignited. Machines and the work area should be frequently cleaned and the waste magnesium kept in covered, clean, dry steel or other noncombustible drums which should be removed from the buildings at regular intervals. Magnesium dust clouds are explosive if an ignition source is present. Grinding equipment should be equipped with a water-spray-type dust precipitator. NFPA 484 requires these types of precipitators to be vented to prevent hydrogen buildup resulting from magnesium reacting with the water spray. NFPA 484 also places restrictions on the mass flow rate of magnesium into the precipitator as well as the amount of magnesium sludge accumulated in the precipitator. The equipment should be restricted to magnesium processing only.

Molten magnesium in the foundry presents a serious fire problem if not properly handled. Sulfur dioxide or melting fluxes are commonly used to prevent oxidation or ignition of magnesium during foundry operations. The action of sulfur dioxide is to exclude air from the surface of the molten magnesium; it is not an extinguishing agent. Fluxes perform both functions.

Pots, crucibles, and ladles that may contact molten magnesium need to be kept dry to prevent steam formation or a violent metal-water reaction. Containers should be checked regularly for any possibility of leakage or weak points. Steel lined runoff pits or pits with tightly fitting steel pans should be provided, and the pans kept free of iron scale. Leaking metal contacting hot iron scale results in a violent thermite reaction. Use of stainless steel pans or linings will eliminate this possibility.

Heat treating ovens or furnaces, where magnesium alloy parts are subjected to high temperatures to modify their properties, present another special problem. Temperatures for heat-treating needed to secure the desired physical properties are often close to the ignition temperatures of the alloys themselves, and careful control of temperatures in all parts of the oven is essential. Hot spots leading to local overheating are a common cause of these fires. Large castings do not ignite readily, but fins or projections on the castings, as well as chips or dust, are more readily subject to ignition. For this reason, castings should be thoroughly cleaned before heat-treating. Magnesium castings in contact with

aluminum in a heat-treating oven will ignite at a lower temperature than when they are placed on a steel car or tray.

Magnesium should not be heat treated in nitrate salt baths. Certain commonly used molten mixtures of nitrates and nitrites can react explosively with magnesium alloys, particularly at temperatures over 538°C (1,000°F).

Extinguishing Magnesium Fires

Magnesium and its alloys present special problems in fire protection. Extinguishment of a magnesium fire should NOT be attempted with the following agents: water, any water-based agent (foams), carbon dioxide, halon containing agents, or nitrogen.

Considering the importance of prompt attack on magnesium fires, automatic sprinklers may be desirable because they provide automatic notification and control of fire. While the water from the sprinklers may have the immediate effect of intensifying magnesium combustion, it will serve to protect the structure and prevent ignition of surrounding combustible material. An excess of water applied to fires in solid magnesium (avoiding puddles of molten metal) cools the metal below the ignition temperature after some initial intensification, and the fire goes out rapidly. By contrast, the fire may be intensified but not controlled with only a small, finely divided water spray.

The method of extinguishing magnesium fires depends largely upon the form of the material. Burning chips, shavings, and small parts need to be smothered and cooled with a suitable dry-chemical extinguishing agent (e.g., graphite and dry sodium chloride). Where magnesium dust is present, care should be taken to prevent a dust cloud from forming in the air during application of the agent because this may result in a dust explosion.

Small fires may be controlled by flooding with helium or argon if the fire is located in an area where flooding would be effective. Inert gases, other than the noble gases (argon, helium, etc.) are ineffective on magnesium fires and some can create dangerous byproducts (magnesium nitride).

Fires in pieces of magnesium can be fought without difficulty if attacked in their early stages. It may be possible to remove surrounding material, leaving the small quantity of magnesium to burn itself out harmlessly.

Magnesium fires in heat-treating ovens can best be controlled with powders and gases developed for use on such fires. By using melting fluxes to exclude air from the burning metal, fires in heat treating furnaces have been successfully extinguished. Boron trifluoride gas is an effective extinguishing agent for small fires in heat-treating furnaces. Cylinders of boron trifluoride can be permanently connected to the oven or mounted on a suitable cart for use as portable equipment. Boron trifluoride is allowed to flow into the oven until the fire is extinguished, or, where large quantities of magnesium are well involved before discovery or where the furnace is not tight, the boron trifluoride will control the fire until flux can be applied to extinguish the fire.

Titanium

Properties

Titanium, like magnesium, is classified as a combustible metal, but again the size and shape of the metal determines largely whether it will ignite. Castings and other pieces of titanium are not combustible under ordinary conditions. Small chips, fine turnings, and dust ignite readily and, once ignited, burn with the release of large quantities of heat. Tests have shown that very thin chips and fine turnings could be ignited by a match and heavier chips and turnings by a Bunsen burner. Coarse chips and turnings 0.79 by 2.7 mm (1/32 by 3/28 in.) or larger may be considered as difficult to ignite, but unless it is known that smaller particles are not mixed with the coarser material in significant amounts, it is wise to assume easy ignition is possible. The unusual conditions under which various shaped pieces of titanium will ignite spontaneously include contact with liquid oxygen, in which case it may explode.

Finely divided titanium in the form of dust clouds or layers does not ignite spontaneously (differing in this respect from zirconium, plutonium, and certain other metals); however, in the presence of an ignition source such as static electricity, titanium fines are easily ignited in air, carbon dioxide, or nitrogen. Ignition temperatures of titanium dust clouds in air range from 332 to 588°C (630 to 1,090°F), and of titanium dust layers from 382 to 510°C (720 to 950°F). Refer to NFPA 484 for additional information.

Storage and Handling

Titanium castings and ingots are so difficult to ignite and burn that special storage recommendations for large pieces are not included in NFPA 484. Titanium sponge and scrap fines, on the other hand, do require special precautions, such as storage in covered metal containers and segregation of the container from combustible materials. Because of the possibility of hydrogen generation in moist scrap and spontaneous heating of scrap wet with animal or vegetable oils, a yard storage area remote from buildings is recommended for scrap that is to be salvaged. Alternate recommended storage locations are detached scrap storage buildings and fire resistive storage rooms. Buildings and rooms for storage of scrap fines should have explosion vents.

Process Hazards

Contact of molten metal with water is the principal hazard during titanium casting. To minimize this hazard, molds are usually thoroughly predried and vacuumed, or inert gas protection is provided to retain accidental spills.

The heat generated during machining, grinding, sawing, and drilling of titanium may be sufficient to ignite the small pieces formed by these operations or to ignite mineral oil base cutting lubricants. Consequently, water-based coolants should be used in ample quantity to remove heat, and cutting tools should be kept sharp. Fines should be removed regularly from work areas and stored in covered metal containers. To prevent titanium dust explosions, any operation that produces dust should be equipped with a dust collecting system discharging into a water-type dust collector.

Descaling baths of mineral acids and molten alkali salts may cause violent reactions with titanium at abnormally high temperatures. Titanium sheets have ignited upon removal from descaling baths. This hazard can be controlled by careful regulation of bath temperatures.

There have been several very severe explosions in titanium melting furnaces. These utilize an electric arc to melt a consumable electrode inside a water-cooled crucible maintained under a high vacuum. Stray arcing between the consumable electrode and crucible, resulting in penetration of the crucible, permits water to enter and react explosively with the molten titanium. Indications are that such explosions approach extreme velocities. The design and operation of these furnaces require special attention in order to prevent explosions and to minimize damage when explosions do occur.

Extinguishing Titanium Fires

Carbon dioxide, foam, and dry chemical extinguishers are not effective on titanium fires, but good results have been obtained with dry powder extinguishing agents developed for use on magnesium fires. The use of water or a water-based agent will result in a violent exothermic reaction.

The safest procedure to follow with a fire involving small quantities of titanium powder is to cover the burning material with an appropriate extinguishing media (e.g. dry sand, MET-L-X or other Na-Cl based agents). Great care should be taken to prevent formation of a titanium dust cloud during the application of the extinguishing agent.

Large titanium fires are very difficult to control or extinguish. Adequate quantities of Class D agent are not likely to be available and if they were, application of the agent to the fire would be a serious safety risk due to the very high burning temperatures of the titanium. Large fires are usually controlled by segregating the fire area and allowing the fire to burn out. Based on the available quantities of titanium, this may result in a fire that burns for several days.

Alkali Metals: Sodium, Potassium, Sodium-Potassium (NaK), and Lithium

Properties

Sodium

At room temperature, sodium oxidizes rapidly in moist air, but spontaneous ignitions have not been reported except when the sodium is in a finely divided form. When heated in dry air, sodium ignites near its boiling point of 880°C (1,616°F). Sodium in normal room air and at a temperature only slightly above its melting point 98°C (208°F) has been ignited by placing sodium oxide particles on its surface. This indicates the possibility of ignition at temperatures below the boiling point. Once ignited, hot sodium burns vigorously and forms dense white clouds of caustic sodium oxide fumes. During combustion, sodium generates about the same amount of heat as an equivalent weight of wood.

The principal fire hazard associated with sodium is the rapid reaction with water. It floats on water (specific gravity 0.97), reacting vigorously and melting. The hydrogen liberated by this reaction may be ignited and explode from the heat of the reaction. Sodium (like other burning, reactive metals) reacts

violently with most chemicals that can oxidize, halogenated hydrocarbons, with halogens such as iodine, and with sulfuric acid.

Potassium

The fire hazard properties of potassium (K) are very similar to those of sodium with the difference that potassium is more reactive. For example, the reaction between potassium and the halogens is more violent, and, in the case of bromine, a deflagration/detonation can occur. There is an explosive reaction with sulfuric acid. Unlike sodium, potassium forms some peroxides and superoxides during combustion. These peroxides may react violently with organic contaminants (oils, etc.). Peroxides and superoxides may also react explosively with metallic potassium (see NaK below). Superoxides of potassium can be shock sensitive.

Sodium-Potassium (NaK)

NaK is the term used when referring to any of several sodium-potassium alloys. The various NaK alloys differ from each other in melting point, but all are liquids or melt near room temperature. NaK alloys possess the same fire hazard properties as those of the component metals except that the reactions are more vigorous. Under pressure, NaK leaks have ignited spontaneously.

The potassium in NaK will react with atmospheric oxygen to form three different oxides, potassium oxide (K_2O), potassium peroxide (K_2O_2), and potassium superoxide (KO_2). These oxides form a crust over the NaK surface. If this crust is permeated and the superoxide (KO_2) is allowed to mix with the potassium in the NaK, a very high temperature thermite-type reaction can occur. This reaction may take several minutes to develop if the NaK is stored under an inert atmosphere or it may occur instantly if stored under atmospheric oxygen.

Lithium

Lithium, like sodium and potassium, cesium, and rubidium is one of the alkali metals. Lithium undergoes many of the same reactions as sodium. For example, both sodium and lithium react with water to form hydrogen; but whereas the sodium-water reaction can generate sufficient heat to ignite the hydrogen, the far less violent lithium-water reaction does not. Lithium ignites and burns vigorously at a temperature of 180°C (356°F), which is near its melting point. Unlike sodium and potassium, it will burn in nitrogen. The caustic (oxide and nitride) fumes accompanying lithium combustion are more profuse and dense than those of other alkali metals burning under similar conditions. Lithium is the lightest of all metals. During combustion, it tends to melt and flow.

Storage and Handling

Because of their reactivity with water, alkali metals require special precautions to prevent contact with moisture. Drums and cases containing alkali metals should be stored in a dry, fire-resistive room or building used exclusively for alkali metal storage. Storage rooms should be located on the first floor level without a basement below the storage room. Since sprinkler protection would be undesirable, no combustible materials should be stored in the same area. It is good practice to store empty as well as filled alkali metal containers in the same area, and all containers should be on skids. There should be no water or steam pipes, but sufficient heat should be maintained to prevent moisture condensation caused by

atmospheric changes. Natural ventilation at a high spot in the room is desirable to vent any hydrogen that may be released by accidental contact of alkali metal with moisture.

Small quantities (1 kg or less per container) of alkali metals should be stored in sealed containers inside of metal or approved hazardous material storage cabinets in a building with fire sprinkler protection. Combustible materials should not be stored adjacent to the storage cabinets

Large quantities of alkali metal are often stored outdoors in aboveground tanks. In such installations, weatherproof enclosures should cover tank manholes and the free space within the tank should contain a nitrogen atmosphere. Argon or helium atmospheres should be substituted for nitrogen in the case of lithium.

For small-scale transfer of solid alkali metal from a storeroom to the use area, a metal container with a tight cover is recommended. Alkali metal should be removed from storage in an area other than the designated storage rooms and in as small quantities as practicable. When stored on workbenches, it should be kept under kerosene or oil in a closed container. Alkali metal, with its great affinity for moisture, may react at the time it is sealed in a container with any atmospheric moisture. Because of the possible presence of hydrogen, containers should not be opened by hammering on the lid.

Process Hazards

Liquid alkali metal is valuable as a high temperature heat transfer medium. For example, it is used in hollow exhaust valve stems in some internal combustion engines and in the transfer of heat from one type of nuclear reactor to a steam generator. In the latter process or other large-scale use of molten alkali metal, any equipment leak may result in a fire. Where molten alkali metal is used in process equipment, steel pans should be located underneath to prevent contact with concrete floors. Contact of molten alkali metal with concrete will cause spalling of the concrete and spattering of the metal.

Processing of alkali metal is essentially remelting it to form sticks or bricks or to add as a liquid to closed transfer systems. During this handling, contact with moist air, water, halogens, halogenated hydrocarbons, and sulfuric acid needs to be avoided.

Extinguishing Fires in Sodium, Lithium, NaK, and Potassium

The common extinguishing agents, such as water, foam, and clean agents, should never be used because of the violent reactions upon application to alkali metals. Class D dry powders developed for alkali metal fires, dry sand, dry sodium chloride, copper powder, and dry soda ash are effective, with graphite based Class D agents being the best. These finely divided materials blanket the fire while the metal cools to below its ignition temperature. Alkali metal burning in an apparatus can usually be extinguished by closing all openings. Blanketing with nitrogen is also effective except for lithium. In the case of lithium, argon or helium atmospheres should be used. If the alkali metal is with a combustible liquid, the Class B agent must be compatible with the Class D agent being used on the fire.

Lithium and lithium alloys used in products such as batteries that also use ordinary combustibles, present an unusual fire hazard as many of the suppressants used to extinguish ordinary combustibles are not compatible with combustible metals. For more information, refer to NFPA 484.

Zirconium and Hafnium

Properties

Zirconium

The combustibility of zirconium increases as the average particle size decreases, but other variables, such as moisture content, also affect its ease of ignition. Pieces of zirconium can withstand extremely high temperatures without igniting, whereas clouds of dust in which the average particle size is 3 microns have ignited at room temperature. Dust clouds of larger particle size can be readily ignited if an ignition source is present, and such explosions can occur in atmospheres of carbon dioxide or nitrogen as well as in air. Zirconium dust will ignite in carbon dioxide at approximately 621°C (1,150°F) and nitrogen at approximately 788°C (1,450°F). Tests have also indicated that layers of 3-micron-diameter dust are susceptible to spontaneous ignition. The depth of the dust layer and its moisture content are important variables for ignition. Spontaneous heating and ignition are also possibilities with scrap chips, borings, and turnings if fine dust is present. Layers of 6-micron-diameter dust have ignited when heated to 190°C (374°F). Combustion of zirconium dust in air is stimulated by the presence of limited amounts of water (5 to 10%). When very finely divided zirconium powder is completely immersed in water, it is difficult to ignite, but once ignited it burns more violently than in air.

Pieces of zirconium do not ignite spontaneously under ordinary conditions, but ignition will occur when an oxide-free surface is exposed to sufficiently high oxygen concentrations and pressure. The explanation for this reaction is the same as that cited for a similar titanium reaction. Zirconium fires (like fires involving titanium and hafnium) attain very high temperatures, but generate very little smoke.

Explosions have occurred while zirconium was being dissolved in a mixture of sulfuric acid and potassium acid sulfate. Zirconium has exploded during and following pickling in nitric acid, and also during treatment with carbon tetrachloride or other halogen-containing materials. Spontaneous explosions have occurred during handling of moist, very finely divided, contaminated zirconium scrap.

Hafnium

Hafnium has similar fire properties to zirconium. Hafnium burns with very little flame, but it releases large quantities of heat. Hafnium in sponge form may ignite spontaneously.

Hafnium is generally considered somewhat more reactive than titanium or zirconium of similar form. Damp hafnium powder reacts with water to form hydrogen gas, but at ordinary temperatures, this reaction is not sufficiently vigorous to cause the hydrogen to ignite. At higher temperatures, however, ignition of the hydrogen may be expected to proceed explosively.

Storage and Handling

Special storage precautions are not required for zirconium castings because of the very high temperatures that the pieces can withstand without igniting. Zirconium powder, on the other hand, is highly combustible; consequently, it is customarily stored and shipped in 3.78-L (1-gal) containers with at least 25% water by volume. For specific details, refer to NFPA 484.

Zirconium powder storerooms should be of fire-resistive construction equipped with explosion vents. Containers should be separated from each other to minimize the possibility of a fire at one can involving others and to permit checking of the cans periodically for corrosion. Consider disposing of cans containing zirconium powder that have been on the shelf for more than six months.

Process Hazards

In general, processing recommendations for zirconium and hafnium are the same. Handling of zirconium powder, whenever possible, should be under an inert liquid or in an inert atmosphere. If zirconium or hafnium powder is handled in air, extreme care needs to be used because the small static charges generated may cause ignition.

To prevent dangerous heating during machining operations, a large flow of mineral oil or water-base coolant is required. In some machining operations, the cutting surface is completely immersed. Turnings should be collected frequently and stored under water in cans. Where zirconium dust is a byproduct, dust-collecting equipment that discharges into a water precipitation type of collector is a necessity. Ignition of hafnium can result in an explosion when moisture content is in the range of 5-10%; it is therefore highly advantageous to ensure that water concentrations are 25% or greater at all times when water is used as part of the process.

Extinguishing Fires in Zirconium and Hafnium

Fires exposing pieces of zirconium can be extinguished with water. Limited tests conducted by Industrial Risk Insurers have indicated that the discharge of water in spray form would have no adverse effect on burning zirconium turnings. These tests showed that when a sprinkler opened directly above an open drum of burning zirconium scrap, there was a brief flare-up, after which the fire continued to burn quietly in the drum. When a straight stream of water at a high rate of flow was discharged into the drum, water overflowed and the fire went out. Similarly, fires exposing pieces of hafnium can also be extinguished with water; however, water should never be used directly on a hafnium fire unless it is used in large quantities.

Where small quantities of zirconium or hafnium powder or fines are burning, the fire can be ringed with a Class D extinguishing powder to prevent its spread, after which the fire can be allowed to burn out. Special powders developed for metal fires have been effective in extinguishing zirconium or hafnium fires. When zirconium or hafnium dust is present, the extinguishing agent should be applied so that a zirconium dust cloud will not form. If the fire is in an enclosed space, it can be smothered by introducing argon or helium.

Calcium and Zinc

Properties

Calcium

The flammability of calcium depends considerably on the amount of moisture in the air. If ignited in moist air, it burns without flowing at a somewhat lower rate than sodium. It decomposes in water to yield calcium hydroxide and hydrogen, which may burn. Finely divided calcium will ignite spontaneously in air. It should be noted that barium and strontium are very similar to calcium in their fire properties.

Zinc

Zinc does not introduce a serious fire hazard in sheets, castings, or other pieces because of the difficulty of ignition. Once ignited, however, large pieces burn vigorously. Moist zinc dust reacts slowly with the water to form hydrogen, and, if sufficient heat is released, ignition of the dust can occur. Zinc dust clouds in air ignite at 599°C (1,110°F). Burning zinc generates appreciable smoke that obscures visibility and could inhibit occupant egress and emergency response.

Storage, Processing, and Extinguishing Fires in Calcium and Zinc

The storage, handling, and processing recommendations for magnesium are generally applicable to calcium and zinc.

Aluminum

The usual forms of aluminum have a sufficiently high ignition temperature so that its burning is not a factor in most fires. However, very fine chips and shavings are occasionally subject to somewhat the same type of combustion as described for magnesium. Powdered or flaked aluminum in its pure form can ignite easily in air and can be explosive in air in the presence of an ignition source (e.g. static discharge). The degree of explosively of aluminum powder or flakes increases as the particle size decreases. Wet or dry dust collection systems may be subject to such fires and protection requirements are established in NFPA 484. Such collection systems should be located outdoors.

Aluminum in contact with magnesium burns readily, perhaps due to the formation of an alloy at the interface. Aluminum pastes are subject to fires, especially when the paste is solvent-wet and the solvent vapors have a low ignition temperature.

Extinguishing agents for aluminum depend upon the form in which it is in. Although a fire in ordinary combustible materials with large castings of aluminum can be suppressed with large quantities of water, fire involving aluminum fines or powder must be treated carefully to avoid dispersal that may result in an explosion. Powder and fines fires are best handled by hand application of dry sand or Class D extinguishing agent appropriate for the metal. Water, dry powder, carbon dioxide, or halogen containing agents should be avoided as they can increase the intensity of the fire or result in a violent reaction.

Iron and Steel

Iron and steel are not usually considered combustible; in pieces (as in structural steel, cast iron parts, etc.), they do not burn in ordinary fires. Steel in the form of fine steel wool or dust may be ignited in the presence of heat from, for example, a torch, yielding a form of sparking rather than actual flaming in most instances. Fires have been reported in piles of steel turnings and other fine scrap that presumably contained some oil and were perhaps contaminated by other materials that facilitated combustion. Spontaneous ignition of water-wetted borings and turnings in closed areas, such as ship hulls, has also been reported. Pure iron has a melting point of 1,535°C (2,795°F). Ordinary structural steel has a melting point of 1,430°C (2,606°F).

Finely divided powders of iron and steel can be dangerous if they are allowed to form a dust cloud or disturbed due to poor housekeeping practices. Iron/steel powder that is allowed to build up on flat surfaces has the potential to cause massive fire balls if the powder is disturbed and allowed to free fall to the floor below.

Plutonium

Plutonium is one of the most widely used pyrophoric materials in the DOE Complex.Some of the most serious fires occurring within the Complex are caused by the ignition of finely divided plutonium particles. Several plutonium compounds are pyrophoric. The radioactive decay of plutonium creates additional concerns such as dispersal of particles in a fire, pressurization of storage containers, and the production of hydrogen gas during decomposition of adsorbed water.

Note: Plutonium-238 can generate as much as 1-Watt/gram due to radioactive decay

Properties

Metal, Oxides, and Oxidation

Large pieces of plutonium metal react slowly with the oxygen in air at room temperature to form plutonium oxides. The rate of oxidation is dependent on a number of factors. These include: (a) temperature; (b) surface area of the reacting metal; (c) oxygen concentration; (d) concentration of moisture and other vapors in the air; (e) the type and extent of alloying; and (f) the presence of a protective oxide layer on the metal surface. The rate of oxidation increases with increases in the first four factors and decreases with the last. Alloying can either increase or decrease the oxidation rate, depending on the alloying metal. Of all these factors, moisture has a large effect on the oxidation rate and is especially significant in evaluating conditions for storing plutonium metal and oxide.

Several plutonium oxides can be formed from oxidation of metal or decomposition of plutonium compounds. Oxide phases corresponding to sesquioxide (Pu_2O_3) and dioxide (PuO_2) compositions have been identified and are well characterized. Pu_2O_3 is pyrophoric in air and rapidly forms plutonium dioxide while releasing heat. The dioxide is unreactive in air, but reportedly, heats slowly with water vapor at elevated temperatures.

Hydride

Plutonium hydride (PuH_x, $2 < x < 3$) forms during corrosion of plutonium metal by hydrogen from water, organic materials, and other sources. Hydride is rapidly oxidized by dry air at room temperature to produce PuO_2 and H_2 and reacts with nitrogen at 250°C (482°F) to form plutonium nitride (PuN). The reactivity of plutonium hydride in air depends on factors such as particle size, presence/absence of protective oxide layer, and the hydrogen to plutonium atomic ratio. Finely divided hydride is pyrophoric in air at room temperature. Thus, the only safe practice is to handle and store hydride in a dry, oxygen-free atmosphere.

Carbides and Nitride

Plutonium carbides, oxycarbides, and nitride are reactive and potentially pyrophoric materials that could pose handling problems if exposed to air or oxygen-containing atmospheres. These compounds react readily with moisture to form gaseous products such as methane, acetylene, and ammonia. Because plutonium compounds of this type have been prepared at several sites and may have been "temporarily" stored under special conditions (hermetically sealed within an inert atmosphere) without first oxidizing them, caution should be exercised in opening cans that might contain such materials.

Reactions Involving Water

Water vapor accelerates the oxidation of plutonium by oxygen and reacts directly with the metal. Oxidation is about ten times higher in humid air than in dry air at room temperature. For this reason, plutonium metal has routinely been handled in a very dry atmosphere such as one with a -40°C (-40°F) dew point. Inerting of gloveboxes and enclosures for handling plutonium with nitrogen or argon is effective in reducing metal oxidation only if it also excludes water vapor. Rapid oxidation does not occur if oxygen is present at a level of 5% in nitrogen or argon. However, if 1.3% moisture (50% relative humidity) accompanies the oxygen, then rapid metal oxidation can be anticipated.

Plutonium dioxide can adsorb water on the surface. The quantity adsorbed is a direct function of the surface area of the oxide. The principal hazard associated with adsorbed water is pressurization of a sealed oxide container through any of several separate processes including evaporation of water, radiolysis to form oxygen and hydrogen, or direct reaction with the oxide to form a higher oxide and hydrogen gas.

Pressurization of oxide containers can be prevented by use of sealed containers fitted with durable, high-efficiency metal filters. Although gases can escape without release of plutonium-containing particles, air (possibly moist) is able to enter the container.

Pyrophoricity

When heated to its ignition temperature, plutonium reacts at an accelerated oxidation rate, which sustains continued oxidation. The burning temperature depends on the rate of heat dissipation to the surroundings and the rate of heat generation, which is dependent on the surface area of oxidizing metal. Temperatures of plutonium fires usually exceed the melting temperature of plutonium metal 640°C (1184°F) which causes the material to consolidate into a molten configuration. As such, finely divided metal, turnings, and casting skulls tend to ignite readily and achieve a high initial temperature that lasts until melting occurs and the surface area is reduced.

The oxide layer that forms during burning limits the oxidation rate of plutonium. The burning process is similar to that of a charcoal briquette. The ignition temperature of plutonium metal depends on the factors that increase the oxidation rate. Finely divided plutonium, such as metal powder or fine machine turnings, ignites near 150°C (302°F). This temperature is easily reached if a coexisting pyrophoric material such as a hydride spontaneously ignites at room temperature. Pieces of plutonium characterized as having a minimum thickness greater than 1.0 mm (0.04 in) and a specific surface area greater than 1 cm^2 /g (71 in^2 lb) requires temperatures in excess of 400°C (752°F) to ignite. Many plutonium fires have occurred because samples containing finely divided metal have spontaneously ignited. Fires have not occurred with well-

characterized metal existing in large pieces that have higher ignition temperatures. Thus, a piece of plutonium is not considered pyrophoric or capable of self-ignition.

An investigation of two instances in which kilogram-sized plutonium pieces were observed to "spontaneously ignite" in air at room temperature showed that they had been exposed to unlimited sources of hydrogen for extended periods, and that the samples were thermally insulated when ignition occurred. The amount of hydride present on these pieces apparently generated sufficient heat to cause ignition. These observations emphasize the need for well-characterized materials.

Storage and Handling

Plutonium should be stored as pure metal (Pu) or in its dioxide (PuO_2) form in a dry, inert or slightly oxidizing atmosphere. The formation of oxide from metal is accompanied by a large volume expansion (up to 70%) which may bulge or breach the primary container. Case studies show that mechanical wedging resulting from this expansion can even breach a second metal container, resulting in localized contamination release and possible exposure of personnel. Oxidation of the metal and rupture of the container by mechanical wedging are prevented if the storage container is hermetically sealed. Plutonium radioactively decays producing alpha particles and helium molecules. Over long-term storage, helium buildup can contribute to the pressurization of containers.

Plutonium sesquioxide and hydride should be converted to plutonium dioxide before storage. Primary and secondary containers should be hermetically sealed and contain no plastics or other materials that decompose as a result of radiation exposure.

For a more complete discussion of plutonium storage, refer to DOE-STD-3013-2012, *Stabilization, Packaging, and Storage of Plutonium-Bearing Materials* (March 2012).

Where plutonium must be handled, placing larger pieces on a thick stainless steel slab will generally conduct heat away from the material fast enough that spontaneous ignition does not occur.

Extinguishing Plutonium Fires

Plutonium fires should not be approached without protective clothing and respirators unless the fire is enclosed in a glovebox. The most effective agent for extinguishing plutonium fires has been found to be magnesium oxide sand. Gloveboxes that contain pyrophoric forms of plutonium should also contain a supply of magnesium oxide sand that is adequate for manual extinguishment. Magnesium oxide sand extinguishes a plutonium fire by providing a heat sink that cools the plutonium below its ignition temperature and by providing a barrier that limits the availability of oxygen. Burning plutonium should be completely covered with the sand to as great a depth as possible. Extinguishment - studies have shown that covering plutonium with one to two inches of magnesium oxide sand, or using a mass of magnesium oxide sand roughly three times that of the plutonium has been effective at extinguishing a plutonium fire. Additionally, if a mass of plutonium is burning within a stainless steel glovebox, agents typically non-compatible with plutonium (Clean Agents, CO2, etc.) can be used on the exterior of the glovebox to cool the burring mass; in some cases, this is sufficient to extinguish a plutonium fire by reducing the temperature of the burning mass below its ignition temperature.

Argon is a very effective extinguishing agent, if the oxygen content in the atmosphere is maintained at 4% or less. Above 4% oxygen, flooding with argon will not extinguish a plutonium fire. This is an important point, since it is nearly impossible to reduce the oxygen content to 4% or less during argon flooding in most fume hoods. Argon may be used effectively to cool the burning plutonium prior to application of the magnesium oxide sand.

Other agents have been tested for use on plutonium fires; however, none has proven to be as effective as magnesium oxide. Typical foam or dry chemical agents are not effective extinguishing agents. Fusible salt agents have been shown to be effective on small-scale plutonium fires. However, the expansion that accompanies the oxidation of plutonium has caused the fusible salt coating to crack, allowing the plutonium to re-ignite.

As a last resort, water can be used as an extinguishing agent for fires of ordinary combustibles that are exposing plutonium. Where criticality safety considerations preclude the introduction of moderators such as water, suitable alternative fire protection measures need to be identified within fire hazard plans to coordinate or incorporate such measures into emergency response activities. Proper housekeeping, which includes removal of combustibles from pyrophoric forms of plutonium, is the most important aspect of fire loss minimization.

Uranium

Properties

Uranium is a radioactive metal that is also combustible in finely divided forms. Its radioactivity does not influence its combustibility, nor is the radioactivity influenced by burning the material. Metallic uranium that is handled in pieces does not present a significant fire risk unless exposed to a severe and prolonged external fire. Once ignited, pieces of metal burn very slowly. In the absence of strong drafts, uranium oxide smoke tends to deposit in the immediate area of the burning metal. Unless covered with oil, pieces of uranium will burn with virtually no visible flame. Burning uranium reacts violently with carbon tetrachloride, 1,1,1-trichloroethane, and the Halons.

Uranium in finely divided form is readily ignitable, and uranium scrap from machining operations is subject to spontaneous ignition. This reaction can usually be avoided by storage under dry (without moisture) oil. Grinding dust has been known to ignite even under water, and fires have occurred spontaneously in drums of coarser scrap after prolonged exposure to moist air. Because of uranium's thermal conductivity, larger pieces generally have to be heated entirely to their ignition temperature before igniting. Moist dust, turnings, and chips react with water to generate hydrogen gas. Uranium surfaces treated with concentrated nitric acid are subject to explosion or spontaneous ignition in air.

The pyrophoric characteristics of uranium are similar to those of plutonium except that uranium forms do not ignite as easily as those of plutonium do. Both form pyrophoric oxides and hydrides. Both react violently with water and are best stored in their oxide form (UO_2, PuO_2) in dry, inert atmospheres. Uranium metal (U) releases hydrogen gas (H_2) when allowed to react with water. The hydrogen may then react with the metal to form uranium hydride (UH_3) which may in turn react with oxygen in the air to form stable uranium oxide (UO_2) and hydrogen gas (H_2).

The heat generated from corrosion, if dissipated in a water storage environment, may not be sufficient enough to ignite the uranium if properly configured. This is a dynamic process and an SME should be consulted for an appropriate hazard analysis.

Storage and Handling

The storage of the many forms of uranium is beyond the scope of this primer. For a more complete discussion of uranium storage, refer to DOE-STD-3028-2000, *Criteria for Packaging and Storing Uranium-233-Bearing Materials* (July 2000).

Extinguishing Uranium Fires

Uranium fires should be extinguished with the same techniques and precautions as plutonium fires (see corresponding paragraph on plutonium).

Combustible Metal Extinguishing Agents and Application Techniques

A variety of metals burn, particularly those in finely divided form. Some metals burn when heated to high temperatures by friction or exposure to external heat; others burn from contact with moisture or in reaction with other materials. Because accidental fires may occur with these materials, it is important to understand the nature of the various fires and the hazards involved.

The hazards involved in the control or complete extinguishing of metal fires include extremely high temperatures, steam explosions, hydrogen explosions, toxic products of combustion, explosive reaction with some common extinguishing agents, breakdowns of some extinguishing agents with the liberation of combustible gases or toxic products of combustion, and, in the case of certain nuclear materials, dangerous radiation. Some agents displace oxygen, especially in confined spaces. Therefore, extinguishing agents and methods for their specific application should be selected with care. Metal fires should not be approached without suitable personal protective equipment, including but not limited to: self-contained breathing apparatus and protective clothing, unless immediate application can be performed to suppress or control a small fire.

The use of water on a combustible metal fire is hazardous and great care must be taken to ensure the application of water does not deleteriously affect the fire. The application of water or a water-based extinguishing agent may result in a violent reaction which has the potential to spread burning material to an adjacent area; this can cause significant safety risk to firefighting personnel or others that may be located near the fire incident.

Numerous agents have been developed to extinguish combustible metal (Class D) fires, but a given agent does not necessarily control or extinguish all metal fires. Although some agents are valuable in working with several metals, other agents are useful in combating only one type of metal fire. Despite their use in industry, some of these agents provide only partial control and cannot be considered actual extinguishing agents. Certain agents that are suitable for other classes of fires should be avoided for metal fires, because violent reactions may result (e.g. water on sodium; vaporizing liquids on magnesium fires).

Certain combustible metal extinguishing agents have been used for years, and their success in handling metal fires has led to the designations "approved extinguishing powder" and "dry powder." These designations have appeared in codes and other publications where it was not possible to employ the proprietary names of the powders. These terms have been accepted in describing extinguishing agents for metal fires and should not be confused with the name "dry chemical," which normally applies to an agent suitable for use on flammable liquid (Class B) and live electrical equipment (Class C) fires. Class B extinguishing agents may not be safely applied to combustible metal (Class D) fires. Other extinguishing agents discussed herein have been used only experimentally in limited areas or at specific installations, and require much judgment in application. NFPA 10 should be used when placing fire extinguishers. Where a hydrophilic (attracts moisture and can chemically bond with it) Class D agent is placed in a container other than a fire extinguisher, it must be in an air-tight container to avoid attracting moisture from the air, which would reduce the effectiveness of the agent.

For fires that occur in chemical processing areas, the use of chemicals involved in the processing can be used to control or extinguish the fire with little or no adverse effect on the chemical processing. For example, Lithium metal is produced in a salt bath of lithium chloride and potassium chloride operating at approximately 450°C (842°F). If a fire should occur in the salt bath, adding more lithium or potassium chloride to the salt bath will lower the temperature of the salt bath and control the “operational excursion.” If an operator was to try to control the fire with a commercial fire extinguisher, the agent could poison the salt bath that would have to be drained, relined, and brought back to operations, which is costly in both downtime and expense. For this reason and others, it is important to ensure an adequate fire hazard plan is in place.

The successful control or extinguishment of metal fires depends heavily upon the method of application, training, and experience. Class D agents are not all effective on all Class D fires and selection must be based on the material being protected. To avoid re-ignition, do not move the remains of a metal fire until it has cooled sufficiently. Personnel using a Class D fire extinguisher or a container containing the Class D agent must be properly trained since the methods differ from conventional Class A:B:C extinguishers. Practice drills should be held on the particular combustible metals on which the agent is expected to be used. Prior knowledge of the capabilities and limitations of agents and associated equipment is always useful in emergencies. **Fire control measures or extinguishing agents must be immediately available to ensure they are effective.** In industrial plant locations where work is performed with combustible metals, public fire departments and industrial fire brigades have the advantage of fire control drills conducted under the guidance of knowledgeable individuals.

Combustible Metal Fire Extinguishing Agents

A number of proprietary combustible metal extinguishing agents have been submitted to testing agencies for approval or listing. Others have not, particularly those agents developed for special metals in rather limited commercial use. Those extinguishing agents described as follows have been shown to be effective for use on fires involving magnesium, aluminum, sodium, potassium, and sodium-potassium alloy. NFPA 484 offers guidance on the selection of the appropriate extinguishing agent for use on combustible and pyrophoric metals in the Table “Combustible Metal Fire-Extinguishing Agents Quick Reference Chart” of Annex A.

Met-L-X and Super-D Powder

These hygroscopic (absorbs water) dry powders, with particle sizes controlled for optimum extinguishing effectiveness, are composed of a sodium chloride base with additives. The additives include tricalcium phosphate to improve flow characteristics and metal stearates for water repellency. A thermoplastic material is added to bind the sodium chloride particles into a solid mass under fire conditions.

Met-L-X and Super-D powder are noncombustible, and secondary fires do not result from its application to burning metal. There are no known health hazards resulting from the use of these agents. They are also nonabrasive and nonconductive.

Stored in sealed containers or extinguishers, Met-L-X and Super-D powder are not subject to decomposition or a change in properties. Periodic replacement of extinguisher charges is unnecessary. Extinguishers range from pressurized portable hand units, pails, cans, wheeled units, and stationary or piped systems. The wheeled units and piped systems employ nitrogen as the propellant. If the agent is stored in pails or cans, other than a fire extinguisher, it is applied either by scooping the material onto the fire or by dumping the agent from the container directly. This method is only appropriate where the combustible metal is found in small quantities. With either extinguishing method, sufficient agent must be applied to completely cover the burning material.

These powders are suitable for fires in solid pieces (such as castings) because of their ability to cling to hot vertical surfaces. To control and then extinguish a metal fire, the nozzle of the extinguisher is fully opened from a safe distance and a layer is cautiously applied over the burning material. Some extinguishers have a low flow application that can be applied to finely divided particles with less risk of dispersal of the dust. Once control is established, the nozzle valve is used to throttle the stream to produce a soft, heavy flow. The metal can then be completely and safely covered from close range with a heavy layer. The heat of the fire causes the powder to cake, forming a crust that excludes air and results in extinguishment.

Met-L-X and Super-D extinguishers are available for fires involving magnesium, sodium, potassium, and NaK. In addition, they have been successfully used where zirconium, uranium, and titanium present serious hazards.

Na-X Powder

This powder was developed to satisfy the need for a low chloride content agent that could be used on sodium Potassium and NaK metal fires. Na-X has a sodium carbonate base with various additives incorporated to render the agent nonhygroscopic (does not absorb moisture) and easily fluidized for use in pressurized extinguishers. It also incorporates an additive which softens and crusts over an exposed surface of burning sodium metal. Na-X is noncombustible, and does not cause secondary fires when applied to burning sodium metal above temperatures ranging from 649 to 816°C (1,200 to 1,500°F). No known health hazard results from the use of this agent on sodium fires, and it is nonabrasive and nonconductive.

Stored in hand portables and wheeled and stationary extinguishers, Na-X is listed by UL for fires involving sodium metal up to a temperatures of 649°C (1,200°F). Na-X has been tested on sodium metal (spills and in depth) at fuel temperatures as high as 816°C (1,500°F). Stored in the supplier's sealed metal pails and extinguishers, Na-X is not subject to decomposition, so periodic replacement of the agent is unnecessary.

Other Combustible Metal Extinguishing Agents

Foundry Flux

In magnesium foundry operations, molten magnesium is protected from contact with air by layers of either molten or crust-type fluxes. These fluxes, which are also used as molten metal cleaning agents, consist of various amounts of potassium chloride, barium chloride, magnesium chloride, sodium chloride, and calcium fluoride. The fluxes are stored in covered steel drums. When applied to burning magnesium, these fluxes melt on the surface of the solid or molten metal, excluding air. The thin layer of protection can be provided by properly applying relatively small amounts of flux.

Fluxes are valuable in extinguishing magnesium spill fires from broken molds or leaking pots and in controlling and extinguishing fires in heat-treating furnaces. In open fires, the flux is applied with a hand scoop or a shovel. Areas of furnaces that are difficult to reach can be coated by means of a flux-throwing device similar to those used to throw concrete onto building forms.

While fluxes would rapidly extinguish chip fires in machine shops, such use is not recommended. The fluxes are hygroscopic and the water picked up from the air, combined with the salt, causes severe rusting of equipment.

Copper Powder

Advances in the science of alternative propulsion systems have led to the development of copper powder as a viable extinguishing agent for combustible metals. Work sponsored by the Naval Sea Systems Command was conducted to evaluate the adequacy of existing lithium fire suppression agents and to develop new agents should deficiencies exist.

Copper powder was found to be superior to known lithium fire extinguishing agents in extinguishing capacity. The dry powder is of uniform particle size and extinguishes a lithium fire more quickly and efficiently than existing agents. The process of extinguishment is by formation of a copper-lithium alloy, which is nonreactive and forms preferentially on the surface of the molten lithium. The alloy becomes an exclusion boundary between air and the molten metal, preventing re-ignition and promoting cooling of the unreacted lithium.

Copper powder can be applied from portable, hand-held extinguishers. The nominal size a hand-held extinguisher is 14 kg (30 lb); 68 and 160 kg (150 and 350 lbs) for wheeled units; and is available in fixed systems as well. Argon is used as the propellant. The method of application is similar to that of other metal fire powders, in that the fuel surface is coated with the copper powder in an initial pass, with a throttled application following once control is achieved. Typical application densities are 3.6 kg (8 lbs) of copper powder per pound of lithium for complete extinguishment of the lithium. An 18-kg (40-lb) lithium fire can be fully controlled in 30 seconds and completely extinguished in 9 minutes. Copper powder also has been used to extinguish magnesium and aluminum fires.

Lith-X/G-Plus Dry Powder

These dry powder agents are composed of a special graphite base with additives. The additives render them free flowing so they can be discharged from an extinguisher. The technique used to extinguish a

metal fire with these agents is the same as that used with NaCl based agents. These powders do not cake or crust over when applied to burning metal. They exclude air and conduct heat away from the burning mass to effect extinguishment. They do not cling to hot metal surfaces, so it is necessary to completely cover the burning metal with the agent.

Both agents will successfully extinguish lithium fires and are suitable for the control and extinguishment of magnesium and zirconium chip fires. Lith-x is also suitable for magnesium, sodium, and potassium zirconium, titanium, and NaK fires.

TMB Liquid

TMB is the chemical abbreviation for trimethoxyboroxine. The agent contains methanol to render it free flowing. It is classed as a flammable liquid for shipping purposes. The liquid is colorless and hydrolyzes readily to form boric acid and methanol. Contact with moist air or other sources of water need to be avoided to prevent hydrolysis.

This agent is applied with a specially adapted 9.5 L (2-1/2 gal) stored pressure extinguisher which delivers either spray or a straight stream. Typical application of TMB to a metal fire yields a heat flash because of the breakdown of the chemical compound and ignition of the methanol. A molten boric oxide coating on the hot metal prevents contact with air. A stream of water may be used to cool the mass as soon as metal flames are no longer visible; this should be done cautiously to avoid rupture of the coating. Indoor application (such as in machine shops) is not recommended because of the large volume of boric oxide smoke produced. Boric oxide is only slightly toxic.

While TMB has been used primarily on magnesium fires, it has shown value in application to fires in zirconium and titanium. Although TMB applied as a spray has been used to control small sodium and sodium-potassium alloy fires, it is not recommended for fires in sodium, sodium-potassium alloy, and lithium. TMB reacts violently with lithium and sodium-potassium alloy. It will extinguish sodium in-depth, but the protective coating formed by the TMB absorbs moisture very rapidly and in time may penetrate through to the sodium, resulting in a violent reaction. Field experience has been limited to aircraft fires.

Pyromet Powder

Pyromet powder is composed of specially processed sodium chloride, diammonium phosphate, protein, and a waterproofing and flow-promoting agent. The powder is discharged under pressure provided by a carbon dioxide gas cartridge. The unit contains 11 kg (25 lb) of powder. The applicator consists of a tubular extension from the control valve, terminating in a cone-shaped nozzle. A mechanism in the nozzle absorbs the discharge pressure by swirling the powder as it is expelled. This enables the operator to let the powder fall gently on the burning metal rather than to scatter burning material under the blast of a jet of powder.

Pyromet has proven effective in handling fires involving sodium, calcium, zirconium, and titanium, as well as magnesium and aluminum in the form of powder or chips.

TEC Powder

TEC (ternary eutectic chloride) powder is a mixture of potassium chloride, sodium chloride, and barium chloride that is effective in extinguishing fires in certain combustible metals. The powder tends to seal the metal, excluding air. On a hot magnesium chip fire its action is similar to that of foundry flux. In tests reported in *Fire Technology*, TEC powder was the most effective salt for control of sodium, potassium, and sodium-potassium alloy fires. TEC should not be used on plutonium, uranium, and alkali metal fires because it is hygroscopic.

Nonproprietary Combustible Metal Extinguishing Agents

Specially formulated extinguishing powders are generally used to suppress fires involving metals. Because of the reaction many metals have with water, sprinklers and the use of other water-based agents are not appropriate and, in some cases, quite dangerous. However, many of the special agents for metal fires are at times unsatisfactory because they are corrosive, applied manually rather than by an extinguishing system, capable of clogging extinguishing nozzles, and expensive. When these specialized proprietary extinguishing agents are undesirable, the following nonproprietary agents may be used.

Talc (Powder)

Talc, which has been used industrially on magnesium fires, acts to control rather than extinguish fire. Talc acts as an insulator to retain the heat of the fire, rather than as a coolant. It does, however, react with burning magnesium to provide a source of oxygen. The addition of organic matter (such as protein) to talc assists in the controlling action, but does not prevent the reaction which releases oxygen to the fire.

Carbon Microspheres

Studies have been undertaken to examine the effectiveness of carbon microspheres or microspheroids to extinguish fires involving alkali metals, such as sodium, sodium-potassium, and lithium. These microspheres are petroleum-coke-based particles with a diameter of approximately 100 to 500 microns. The particles possess high thermal conductivity, chemical inertness, and excellent flow characteristics and are capable of being directed onto fires from dry-chemical-type extinguishers and conventional nozzles.

Tests have shown that carbon microspheres compare favorably in performance to other metal extinguishing agents. In particular, experiments with carbon microspheroids incorporating neutron absorbers have been effective in extinguishing fires involving nuclear fissionable materials, such as uranium metal powder. The excellent flow characteristics and noncoking properties of these microspheres suggest an effective way to extinguish radioactive metal fires within the inert atmosphere glovebox enclosures used in the nuclear industry.

Graphite Powder

Graphite powder (plumbago, G-Plus Dry Powder) has been used as an extinguishing agent for metal fires and acts as a coolant. Unless the powder is finely divided and closely packed over the burning metal, some air does get through to the metal and extinguishment is not as rapid as with G-1 powder.

Sand

Dry sand has often been recommended as an agent for controlling and extinguishing metal fires. At times it seems to be satisfactory, but usually hot metal (such as magnesium) obtains oxygen from the silicone dioxide in the sand and continues to burn under the pile. Sand is seldom completely dry. Burning metal reacting with the moisture in the sand produces steam and, under certain conditions, may produce an explosive metal-water reaction. By laying the sand around the perimeter of the fire, fine dry sand can be used to isolate incipient fires of aluminum dust.

Cast Iron Borings

Cast iron borings or turnings are frequently available in the same machine shop as the various combustible metals. Clean iron borings applied over a magnesium chip fire cool the hot metal and help extinguish the fire. This agent is used by some shops for handling small fires where, with normal good housekeeping, only a few combustible metal chips are involved. Contamination of the metal chips with iron may be an economic problem. Oxidized iron chips need to be avoided to prevent possible thermite reaction with the hot metal, and the iron chips need to be free from moisture.

Sodium Chloride

Alkali metal fires can be extinguished by sodium chloride, which forms a protective blanket that excludes air over the metal so that the metal cools below its burning temperature. Sodium chloride is an agent that is used for extinguishing sodium and potassium fires. It can also be used to extinguish magnesium fires.

Soda Ash

Sodium carbonate or soda ash (not dry chemical) is recommended for extinguishing sodium and potassium fires. Its action is similar to that of sodium chloride.

Lithium Chloride

Lithium chloride is an effective extinguishing agent for lithium metal fires. However, its use should be limited to specialized applications because the chemical is hygroscopic to a degree and may present problems because of the reaction between the moisture and the lithium.

Dolomite

If zirconium or titanium in the form of dry powder becomes ignited, neither can be extinguished easily. Control can be affected by spreading dolomite (a carbonate of calcium and magnesium) around the burning area and then adding more powder until the burning pile is completely covered.

Boron Trifluoride and Boron Trichloride

Boron trifluoride and boron trichloride have both been used to control fires in heat-treating furnaces containing magnesium. The fluoride is considerably more effective. In the case of small fires, the gases provide complete extinguishment. In the case of large fires, the gases effect control over the flames and rapid burning, but reignition of the hot metal takes place on exposure to air. A combined attack of boron trifluoride gas followed by application of foundry flux completely extinguishes the fire. For details of gas application, see NFPA 484.

Inert Gases

In some cases, inert gases (such as argon and helium) will control zirconium fires if they can be used under conditions that will exclude air. Gas blanketing with argon has been effective in controlling lithium, sodium, and potassium fires. Caution should be exercised when using the agent in confined spaces because of the danger of suffocation of personnel.

Water

When burning metals are spattered with limited amounts of water, the hot metal extracts oxygen from the water and promotes combustion. At the same time, hydrogen is released in a free state and ignites readily. Since small amounts of water do accelerate combustible metal fires (particularly where chips or other fines are involved), use of common portable extinguishers containing water is not recommended except to control fires in adjacent Class A materials.

Water, however, is a good coolant and can be used on some combustible metals under proper conditions and applications to reduce the temperature of the burning metals below the ignition point. The following paragraphs discuss the advantages and limitations of using water on fires involving various combustible metals.

Sodium, Potassium, Lithium, NaK, Barium, Calcium, and Strontium Fires – Water cannot be used on fires involving these metals. Water applied to sodium, potassium, lithium, sodium-potassium alloys (NaK), barium, calcium, and strontium will induce chemical reactions that can lead to fire or explosion even at room temperatures.

Zirconium Fires – Powdered zirconium wet with water is more difficult to ignite than the dry powder. However, once ignition takes place, wet powder burns more violently than dry powder. Powder containing about 5 to 10% water is considered to be the most dangerous. Water should not be applied to burning zirconium since violent reactions may result.

Plutonium, Uranium, and Thorium Fires – As a last resort, water can be used as an extinguishing agent for fires of ordinary combustibles that are exposing these metals. Where criticality safety considerations preclude the introduction of moderators such as water, suitable alternative fire protection measures need to be identified within fire hazard plans to coordinate or incorporate such measures into emergency response activities.

Magnesium Fires – Automatic sprinklers will extinguish a typical shop fire where the quantity of magnesium is limited. However, water should not be used on any fire involving magnesium - a few burning chips can be extinguished by dropping them into a bucket of water.

Burning magnesium parts such as castings and fabricated structures can be cooled and extinguished with coarse streams of water applied with standard fire hoses. A straight stream scatters the fire, but coarse drops (produced by a fixed nozzle operating at a distance or by use of an adjustable nozzle) flow over and cool the unburned metal. Some temporary acceleration normally takes place with this procedure, but rapid extinguishment follows if the technique is pursued. Well-advanced fires in several hundred pounds (100 lb equals 45 kg) of magnesium scrap have been extinguished in less than 1 minute with two 37.5 mm (1-1/2

in.) fire hoses. Water fog, on the other hand, tends to accelerate rather than cool such a fire. Application of water to magnesium fires needs to be avoided where quantities of molten metal are likely to be present; the steam formation and possible metal-water reactions may be explosive.

Titanium Fires – Water cannot be used on fires in titanium fines and should be used with caution on other titanium fires. Small amounts of burning titanium (other than fines) can be extinguished and considerable salvage realized by quickly dumping the burning material into a large volume of water to completely submerge it. Hose streams have been used effectively on fires in outside piles of scrap, but violent reactions have been reported in other cases where water was applied to hot or burning titanium, resulting in serious injury to personnel. Additional information on the use of water on titanium fires can be found in NFPA 484.

LABORATORY SCALE OPERATIONS

Laboratory operations routinely use small quantities - less than 0.23 kg (1/2 lb) of reactive materials including spontaneously ignitable and pyrophoric chemicals (reagents). Safe handling of these chemicals is critical to the prevention of fires within laboratories and the prevention of injuries to laboratory personnel.

Types of pyrophoric reagents include:

- Alkali metals – Some alkali earth metals and other pure metals that are finely divided (metal catalysts, small particulates and nanoparticles) react with water vapor to generate hydrogen and heat.
- Metal hydrides – These react in the same manner as alkali metals, generating heat and hydrogen.
- Organometallics – These are reagents with carbon metal bonds that generate a volatile organic compound and heat when they react with moisture. The most common examples are alkyl lithium reagents, Gringards (C-MgX), and phosphines. Some compounds that have carbon transition metal bonds are also known as pyrophoric reagents.

There have been several fire events in laboratories both within and outside the DOE Complex that have occurred over the last 20 years that could have been prevented if the pyrophoric reagents were handled properly. The consequences of these events have ranged from minor to significant, including at least one fatality. The 2015 edition of NFPA 45, *Standard on Fire Protection for Laboratories Using Chemicals* has requirements to address the safe handling of pyrophoric reagents to prevent fires and to minimize the risk of significant injury from accidents involving pyrophoric reagents. The following information is intended to address safe handling of pyrophoric reagents.

Operations involving solid reagents are typically performed in an inert atmosphere glovebox or glovebag. Argon is primarily used as the inerting gas in a glovebox/bag arrangement that usually includes an oxygen sensor to verify that oxygen is not present when pyrophoric reagents are in use. Liquid reagents can be used in an inert atmosphere within a glovebox/bag. Pyrophoric liquids that are used outside of an inert atmosphere glovebox/bag have to be handled in closed systems that have been inerted and include an appropriate transfer method.

After operations with pyrophoric reagents have been completed, all laboratory equipment and waste materials that have been in contact with pyrophoric reagents need to be neutralized or passivated to prevent a fire. Very small quantities (microscopic) of pyrophoric reagents will react with oxygen and/or moisture in air and the resulting heat of reaction can start a fire. Most fires associated with laboratory operations with pyrophoric reagents has been caused by inadequate neutralization or passivation of test tubes, glass ware, spatulas, wipes, needles, tubing and other tools prior to exposing them to air. Neutralize pyrophoric liquids in accordance with manufacturer's recommendations, typically by wetting the surfaces of the test tubes, glassware, needles and tubing with a solvent and rinsing with a secondary solvent. For pyrophoric solids, the passivation of wipes, spatulas and other tools can be performed by slowly exposing them to low concentrations of oxygen over a 24-hour period.

Laboratory incidents involving pyrophoric reagents are provided at the end of this Handbook. Additionally, there have been three minor events described below that were caused by pyrophoric waste that was not

properly neutralize/passivated prior to disposal at DOE labs:

- Paper in a garbage can was smoldering in a lab and was extinguished with water. The event was caused by an exothermic reaction that occurred when the residue of chemical slurry containing ethylhexylcarbazole and platinum-loaded carbon in a pipette dried out and reacted with the air to create heat (PNNL Non ORPS-reportable Event).
- Research staff was investigating a burning odor when they found a smoldering chemical wipe in a trash receptacle inside the lab. The smoldering chemical wipe was extinguished with water. The smoldering chemical wipe was a result of a chemical reaction after the wipe was used to clean Raney nickel slurry from a metal spatula and the wipe was discarded in the trash. An investigation uncovered the fact that Raney nickel is provided in slurry with water because, when it is dry, it is a pyrophoric reagent that undergoes an exothermic reaction upon contact with air (PNNL Non ORPS-reportable Event).
- A researcher found a burned trash can in a lab and used water to quench the smoldering papers. The cause of the burned trash can was determined be the result of the disposal of several chemical wipes that were removed from an inert atmosphere glovebox without being passivated. The glovebox was used to handle less than 10-micron size metal powders. The metal powder is pyrophoric when exposed to air and the heat of reaction ignited the chemical wipes (see ORPS report: SC-PNSO-PNNL-PNNLBOPER-2014-0005).

Recommendations for the safe handling of pyrophoric reagents includes but not limited to:

- Personal protective equipment that should be worn when working with pyrophoric reagents outside of an inert atmosphere of a glovebox typically include fire retardant lab coats, fire retardant gloves, safety glasses, and a face shield.
- Operations involving pyrophoric reagents are to be performed only by those with experience in their hazards and properties or under close supervision by those with experience in their hazards and properties.
- Avoid working alone with pyrophoric reagents.
- Handle pyrophoric reagents in systems or enclosures that prevent the chemicals from igniting in accordance with the Safety Data Sheet. Use septum sealed bottles and sealed vessels when pyrophoric liquids are dispensed in a fume hood. Use syringe or double tipped needles to transfer pyrophoric liquids between containers in accordance with manufacturer's recommendations and established safety practices. Glassware, reaction vessels, needles, and other lab equipment must be cleaned of residual moisture and contaminates, and purged with a high purity inert gas prior to use with pyrophoric reagents.
- Use an inert atmosphere glovebox for open dispensing of pyrophoric liquids or handling of pyrophoric solids.
- Passivate or neutralize test tubes, glass ware, spatulas, wipes, needles, tubing and other tools that have been in contact with pyrophoric reagents prior to removing them from an inert atmosphere or disposal in accordance with established safety practices and the recommendations in the chemical's Safety Data Sheet.

INCIDENT CASE STUDIES

Current Edition (2014) Case Studies

The following case studies are considered as an update to the previous handbook Edition and are not inclusive of all DOE spontaneous heating or pyrophoric events that have occurred within the DOE complex between updates. For more information on these events, please access the applicable Occurrence Reporting and Processing System (ORPS) number through either the internet or the ORPS Administrator. For additional case studies, please refer to the NFPA web site listed the bibliography section of this Handbook.

Laboratory (Reagent) Incident – National Renewable Energy Laboratory (2002)

ORPS Report No.: GO-NREL--NREL-2002-0001

At approximately 1301 (MST) on December 27, 2002 a fire was discovered by facility maintenance personnel in a chemical fume hood located in Solar Energy Research Facility (SERF) Lab C-221. The building fire alarm system and the NREL Emergency Notification System were activated. An orderly evacuation of the facility was completed. Firefighters and equipment responded to the scene and assessed the situation. The assessment determined that the fire was contained within the chemical fume hood and that a variety of chemicals, albeit small amounts, was involved. A small flow of liquid was observed coming from the hood and pooling on the floor of the lab. The liquid was identified as de-ionized water, which was leaking from plastic piping that was apparently damaged by the fire. The single most likely cause appears to have been a delayed reaction involving unreacted pyrophoric material, tris (trimethylsilyl) phosphine (TTMSP), inside one or more of the pipettes that had been transferred from the glovebox to the chemical fume hood. Pipettes are used to transfer pyrophoric materials during sample preparation inside the glovebox. The glovebox is maintained under an inert atmosphere (helium) to prevent the reaction of pyrophoric materials. There is no fire detection or suppression system inside the hood. The laboratory is equipped with a fire sprinkler system. This system did not activate, as the fire did not escape the hood. Passive fire protection features such as laboratory compartmentalization and ventilation configuration prevented the spread of smoke beyond the laboratory.

Environmental Restoration Incident – Rocky Flats Environmental Technology Site (2004)

ORPS Report No.: EM-RFO--KHLL-371OPS-2003-0011

On May 6, 2003, D&D activities were taking place in room 2325 in Building 371. Specific actions included cutting sheet metal panels from glovebox 8 to provide an airflow path in an attempt to provide ventilation into the glovebox to reduce airborne levels of plutonium during subsequent clean out and size reduction of the glovebox. Workers noted smoke and evidence of a fire inside the glovebox structure, and took actions in an attempt to control the situation. The workers discharged a number of portable fire extinguishers into the glovebox, only to have the fire re-ignite. Concurrent with these actions, the job supervisor notified the facility Configuration Control Authority (CCA) of the event, who contacted the Fire Department, initiating their response. Further attempts to control the situation were initiated by the workers until the Fire Department arrived on scene and, using water, extinguished the fire and stabilized the situation. Actual

damage to the glovebox and other equipment was minimal, however four of the fire fighters received skin contamination as a result of the firefighting efforts. Because of the use of respirators, they did not receive any radioactive material uptake or significant dose (maximum of 20 mrem). Bioassay analysis of other potentially affected building personnel did not show any significant personnel contamination or radioactive material uptakes.

Environmental Restoration Incident – Idaho National Laboratory (2004)

ORPS Report No.: EM-ID--CWI-ICDF-2005-0004

On September 20, 2005, at the Idaho National Laboratory CERCLA disposal facility, a worker was preparing to mix zinc powder with sulfamic acid in a 5-gallon bucket to be used for treating mercury-contaminated soil when flames erupted from the bucket. A co-worker extinguished the flames using MET-L-X, and all employees left the area. The fire department verified that the fire was out, and no one was injured.

Processing Maintenance Incident – Y-12 (2005)

ORPS Report No.: NA--YSO-BWXT-Y12NUCLEAR-2005-0036

On November 22, 2005, at Y-12, workers were performing maintenance on a crusher-grinder when finely divided material ignited unexpectedly. Thirteen employees were evacuated from the facility. An investigation team learned that several factors caused the fire: the material had been exposed to air for six weeks; actuation of the crusher cylinders stirred up the material, exposing the unoxidated material beneath a layer of passivated material; and the material had been exposed to moisture. One of the employees was transported to an offsite medical facility for observation; the rest were uninjured.

Laboratory (Reagent) Incident – Los Alamos National Laboratory (2005)

ORPS Report No: NA--LASO-LANLFIRNGHELAB-2005-0012

On December 8, 2005, at Los Alamos National Laboratory, a worker in an explosives laboratory was handling a piece of fiberglass matting which was coated with 1 gram of a nanoaluminum-fluoroelastomer mixture when it unexpectedly ignited, causing second-degree burns on the worker's right hand. The mat that ignited was one of a group of mats to which the mixture had been applied, vacuum-dried at 80°C, and cooled to near room temperature. Although facility personnel had worked with this mixture before, they had never used it bonded to fiberglass matting. The accident investigation team determined that the most likely ignition source was energetic buildup within the material and that the hazards of handling the nanoaluminum material had not been properly characterized.

Laboratory (Reagent) Incident - Savannah River National Laboratory (2006)

ORPS Report No.: EM-SR--WSRC-LTA-2006-0002

On January 10, 2006, at Savannah River National Laboratory, a principal investigator and first-line manager were cleaning an attritor mill vessel (shown in Figure 1-1 on a lifting table) when a fire flashed and caused first- and second-degree burns to the right side of the manager's face and head and his left hand. The manager was treated at a local hospital and released.

The attritor mill had been used to blend and finely grind metal hydride into powder for use in hydrogen storage technologies. Grinding the metal hydride into fine particles renders it pyrophoric (i.e., capable of spontaneously combusting in air) because its increased surface area oxidizes more readily.

After preparing the necessary quantity of metal hydride powder, the principal investigator and manager wiped down the attritor mill several times in an argon-inerted glovebox. They then removed the vessel from the glovebox and began wiping it down with isopropyl alcohol. When the vessel was taken out of the glovebox, residual particulate reacted and flashed. The principal investigator extinguished the fire with MET-L-X® powder.

Following its evaluation of the January 2006 fire, the Accident Investigation Board determined that it occurred when metal hydride powder in the vessel bolt holes reacted with air and isopropyl alcohol vapors. The root cause was the failure to fully analyze the hazards of working with metal hydrides, particularly cleanup activities after processing.

Processing Incident – Y-12 (2005)

ORPS Report No.: NA--YSO-BWXT-Y12NUCLEAR-2007-0012

On March 15, 2007, at about 9:15 a.m., a uranium machine turnings (chips) fire occurred during a dry chip transfer operation in Building 9204-2E. The fire was small (~210 g U), was self-extinguished, and did not activate any fire alarms or automatic suppression systems. The operation occurred just outside the linear glovebox laboratory hood. Three assembly operators and their supervisor were involved in the activity, and a Radiological Control technician was in support. The resulting smoke prompted evacuation by involved operators, support personnel, and building occupants. Smoke generated from the fire quickly dispersed. Radiological exposure to the maximally exposed individual may have exceeded the company administrative control level, but is not expected to exceed any regulatory exposure limits.

Laboratory (Reagent) Incident - Pacific Northwest National Laboratory (2013)

Researchers in the Applied Process and Engineering Laboratory were testing a method to decompose ammonia borane (AB) and release hydrogen for use in fuel cells. They created an experimental apparatus that used a slurry of AB powder mixed in silicon oil and tried various methods of pumping the mixture through a metal tube (reactor) wrapped with heat tape to release the hydrogen. Plugging was a problem and they took the apparatus apart and cleaned it after each test. During the third test, at 150C, they noticed the syringe pump was skipping--indicating that the tube was plugged. They stopped the test according to operating procedure and noticed a foam-like substance leaking from a Teflon coupling (circled at right). As the foam bubbled and dripped to the floor of the hood, it was burning with a short, green-colored flame. They shut down power to all heater equipment, put out the flame with a fire extinguisher, and called 375-2400. Lessons Learned: When developing standard operating procedures (SOPs) and obtaining a chemical process permit (CPP), include planned procedures for emergency response for all potential byproducts and, especially any that may be hazardous, despite a low probability of occurrence. This should always include pulling the fire alarm before using a fire extinguisher to put out a small fire.

Laboratory (Reagent) Incident - Argonne National Laboratory East (2014)

ORPS Report No.: SC--ASO-ANLE-ANLECSE-2014-0001

On February 20, 2014 at Argonne National Laboratory East, a worker had finished quenching residual material from a reactive material synthesis in an atmosphere-controlled glovebox. Believing that all the reactants were either removed or quenched, the worker moved the vials, pipettes and wipes to a hood to be rinsed out and disposed of. When the worker opened the last vial, he did not notice any reaction occurring so he started to rinse out the vial with Isopropyl alcohol. Upon contact, the isopropyl alcohol ignited with the fire traveling up the solvent stream and involving all other ignitables within the hood. The fire set off smoke alarms in the lab, alerting the fire department and evacuating the facility. Upon investigation it was theorized that stearic acid must have somehow not come in contact with the remaining reactive material. One reactive by-product that was believed to remain was iron diamide, which reacted with the Isopropyl alcohol causing enough heat to ignite the combustible materials within the hood.

Previous Edition (1994) Case studies

Silane Gas Cabinet Fire

A 6.1 x 9.1 m (20 x 30 ft) room with concrete block walls was used for distribution of process gases to clean room areas. Silane cylinders were located in 12-gauge metal gas cabinets. The ventilation system for the cabinets was in the process of being upgraded and automatic sprinklers protected the cabinets.

The silane cylinder involved was installed about 30 minutes prior to the incident. Employees in the area heard a loud "pop" from the process gas distribution room. Upon investigation, they found the windows of the cabinet broken, the doors open, and fire coming from the cylinder valve. The sprinkler activated properly and confined the fire to the cylinder head.

The escaping silane was caused by an improper connection of the cylinder to the distribution piping. There was evidence that the connection was cross-threaded, allowing the leakage. The flow of silane could not be shut off because of damage to the cylinder manifold connections. The fire continued to burn for about 8-1/2 hours until all silane in the cylinder had been consumed.

Coal Fire at a DOE Site

In 1992, a DOE site experienced a coal fire initiated by spontaneous ignition. Because of the nature of the fire and initial ineffectiveness of the means used to fight it, the fire required more than 28 hours to completely extinguish from the time a hot spot was first detected in a coal bunker. The initial strategy involved trying to remove coal from the bunker by feeding it more rapidly to the boiler and by using a drag chain to move more of it to the field. The drag chain failed in 30 minutes, however. Subsequent efforts to control the fire with carbon dioxide applied through inspection ports at the bottom of the bunker and from the tripper (switchgear) room high above the bunker were ineffective, and may have worsened the situation. The drag chain emptying coal from the bunker worked intermittently after being repaired, and finally stopped. Boiler plant personnel then began to remove burning coal by hand shovel.

Twenty-one hours after the fire was discovered, it had involved a large amount of the bunker. At one point, flames appeared at the tripper room windows, which were approximately 22.86 m (75 ft) above the seat of the hot spots. A strong concern for a steam explosion delayed the application of water, but the decision was finally made to use water, which was applied without incident and eventually ended the fire.

Zirconium Incidents (Smith, 1956)

Up to May 1955, no serious fires had been encountered during storage of scrap zirconium turnings, chips, plates, rods, etc. Such scrap had been stored (pending contemplated future recovery) in segregated open-top bins. Several days after a heavy rain, a fire of unknown origin took place in one of the bins with flames extending 30.48 m (100 ft) into the air. Shortly afterwards, contents of other (but not necessarily adjoining) bins suddenly and intermittently flared up. Material in all bins soon became involved and 72,121 kg (159,000 lb) of zirconium were consumed. The heat was sufficiently intense to crack windows and ignite wood located over 45.72 m (150 ft) away. Particles of burning zirconium were carried over one-quarter mile through the air.

In 1951, some water-wet scrap zirconium powder in wooden barrels was placed in outside storage pending development of scrap-recovery processes. During the next several years, a few minor spontaneous fires broke out in this material. In January 1956, the material in several deteriorated wooden barrels was wet with water and repackaged in steel drums. In May 1956, employees working in the area noted that one of the steel drums lying on its side contained a black material "similar to carbon dust." What happened is uncertain, but a spontaneous explosion occurred accompanied by streaks of red fire with black smoke extending 30.48 m (100 ft) into the air. A pronounced concussion wave was noted and the sound of the blast was heard several miles away. Two employees were killed; one having been blown 24.38 m (80 ft) through the air, and a third lost an arm. The drum contained zirconium, probably in the form of a fine powder. Using extensive precautions, the remaining drums of scrap zirconium were subsequently burned. During this operation, one of the drums exploded.

Two men died and two others were seriously injured in 1954 in a spontaneous explosion initiated during removal of the friction-top lid from a polythene-bag-lined, 3.79 L (1 gal) metal can containing zirconium powder 16 percent wet with water. A ball of flame enveloped the entire area, accompanied by a concussion wave.

A .907 kg (2 lb) sample of carbon-tetrachloride-moistened powdered zirconium was placed in a glass flask, vacuum applied, and the flask very gently heated with a Bunsen burner. The zirconium suddenly began to heat up and detonated with a blinding flash. The explosion was attributed to a small amount of water.

Uranium Incidents (Smith, 1956)

In January 1955, an attempt was made to roll two 453.6 kg (1,000 lb) uranium slabs into 0.254 mm (0.01 in) thick strips. After initial heating to 621°C1 (1,150°F) in a lithium-carbonate-potassium/carbonate salt bath, several 30 percent reductions were made by rolling. It was observed that heavy work passes had caused overheating. The strip, then 19.05 mm (3/4 in) thick, was cooled to 648.89 °C (1,200 °F). The strip again excessively heated during the next three reductions and became so ductile on entering the fourth that it

pulled into two parts. The strip at this stage was cherry red, but by the time it had been removed to the mill floor it was observed to increase in temperature to a white heat followed by melting and burning.

In February 1956, a technician was attempting to roll a plate consisting of zirconium-clad uranium, which, in turn, was clad in a low-carbon-steel jacket. During preheating, the furnace temperature control [which had been set to 788°C (1,450°F)] failed, allowing the temperature to rise to 982°C (1,800°F).

During subsequent rolling, molten iron - zirconium eutectic alloy within the steel jacket was forced to one end of the strip where it burst into flames as it sprayed out over an area approximately 3.048 m (10 ft) wide, 3.048 m (10 ft) high, and 7.62 m (25 ft) long. One employee was seriously injured.

In the early program for the large-scale manufacture of metallic uranium, fine powder was allowed to collect under roughly 7.62 m (25 ft) feet of water. At approximately one-month intervals, and without prior warning, a geyser about 9.14 m (30 ft) high would suddenly develop over the powder and then immediately subside.

A series of cases is known in which pieces of metallic uranium, plutonium, and thorium have displayed unusual pyrophoricity, e.g., spontaneously igniting at room temperature. Spontaneous fires in uranium chips are, however, much more common and in one case ignition occurred six months after the chips had been placed in storage. One investigator of spontaneous fires in briquette uranium chips opened a drum filled with briquettes that had been in outside storage for several weeks. After noting that the drum contents were normal and at approximately room temperature, he was warned by an operator to stand back. A few seconds later, a flame shot to a height of about 7.62 m (25 ft) and then immediately subsided. Upon reinspecting the drum interior, he noted that all of the briquettes were at an incandescent temperature.

A series of incidents have been experienced in which uranium and titanium alloys have displayed explosive surface films following acid treatment. Studies at Argonne National Laboratory showed that such explosions could be averted through use of adequate fluoride ion concentrations in nitric acid etching baths. Witnesses have described metal-surface explosions of this type as involving a brilliant flash of white light, accompanied by a sound similar to that of a 22-caliber rifle shot.

Thorium Incidents (Smith, 1956)

For several years scrap thorium powder had been disposed of by burning in successive small amounts. In July 1956, employees were engaged in burning scrap thorium powder that had previously been washed with several aqueous solutions and vacuum-dried 3 days earlier. Some of the thorium was placed in a special hood and ignited without incident. An employee took a "golf-ball-size" piece of thorium from a metal pail containing 13.61/18.14 kg (30/40 lbs), replaced the pail lid, and placed the piece on a small thorium fire. An immediate sharp explosion blew the employee 6.096 m (20 ft) across the room. Almost immediately, a second blast involving the thorium in the pail was accompanied by a jet of orange fire and big cloud of dust. A third explosion occurred in a nearby vacuum dryer containing about 3.18 Kg (7 lbs) of moist thorium powder. One employee suffered fatal burns, while three others suffered serious injuries.

In preparing an experimental charge for making metallic thorium in a reduction bomb, a mixer was being used to blend metallic calcium, dry zinc chloride, and dry thorium fluoride. After several revolutions of the mixer, the operator opened the mixer vent and, noting the dust and gas were escaping, decided to call his foreman. A second operator closed the vent, started the mixer, and soon heard a rumbling noise, followed by a sudden burst of flame covering a 45 angle and extending parallel to the floor for 12.19 m (40 ft). Of the eight persons injured by the blaze, two subsequently died. Reason for initiation of the reduction reaction in the blender is uncertain and unprecedented. It was subsequently found that the calcium used was particularly reactive.

Miscellaneous Incidents (Smith, 1956)

On June 16, 1954, employees of a high-energy-fuel laboratory were sampling 15 drums of "bag fines" magnesium powder, which were opened in a special room that had been purged with nitrogen until the oxygen content had dropped below 1 percent. During sampling of the fifth drum, the powder ignited suddenly. The flame shot out from the drum, immediately subsided, and the operators left the room after replacing the drum cover. From an external observation window, the employees noticed a gradual darkening of the drum's exterior, moving down to within 50.8 to 101.6 mm (2 to 4 in) of the drum bottom. The following day the drum was opened and contained a definite yellow coloration, which was presumed due to formation of magnesium nitride.

A massive block of metallic barium was cut into 19.05 mm (3/4 in) square pieces while submerged in kerosene. During attempts to remove residual kerosene with carbon tetrachloride (an operation that had been performed many times before without incident), a violent reaction dispersed glass fragments and burning barium over the immediate area. Similar explosions have also occurred when sodium, uranium, and zirconium were treated with carbon tetrachloride.

Trouble had been experienced in getting a Kroll process reduction of zirconium chloride, with magnesium to go to completion. When the furnace was opened up, a slate grey material was noted on the surface, which was thought to consist of zirconium, magnesium, and magnesium chloride. A sample of this material, roughly 6.36 mm (1/4 in) thick and 203.2mm (8 in) square, was removed for test and was totally inert when scratched with a file or hit with a hammer. A piece of the sample melted under an oxyacetylene flame but showed no pyrophoric properties. Samples were then placed in water and a slight evolution of gas was noted. The following day an attempt was made to further wash the samples in several changes of water. While under 127 mm (5 in) of water and without any prior evidence of reaction, an explosion occurred that shattered the laboratory bench, threw the technician against the wall, and blew out a window 7.62 m (25 ft) away. Portions of the water-washed sample blown to the floor ignited and "spit" when stepped upon. Small samples were subsequently tested and found to contain magnesium, zirconium, and 1 percent carbon.

Rocky Flats Plant Fire, 1969

On May 11, 1969, Rocky Flats Plant experienced the worst accident in plant history, a major fire in the 776-777 building, initially caused by pyrophoric plutonium scrap. One of the costliest industrial fires of all time—damages were estimated at between $26 to $50 million dollars—this accident was intensified and confounded by a number of operational errors.

The fire at 2:27 p.m. Sunday was reportedly caused by spontaneous ignition of a 1.5 kg (3.3 lb) briquette of plutonium alloy scrap contained in a metal can. This scrap was believed to have been oily and coated with residual CCl4 (carbon tetrachloride). Once ignited, the fire spread through several hundred interconnected gloveboxes in the two connected buildings.

The fire started in the west end of the north line, progressed eastward, crossed over to the south line through the interconnecting boxes, and spread through the south line. The fire spread through the machining boxes at the east end of 776 and into the inspection boxes in 777. Damage was extensive. Both Benelex, a combustible neutron shielding material added to the gloveboxes, and the combustible Plexiglas glovebox windows contributed to rapid spread of the fire.

The main fire lasted about four hours, with minor flare-ups occurring through the next night. After futile attempts to control the fire with conventional procedures, the firemen finally resorted to the unorthodox procedure of applying water to bring the fire under control. This was the first time in history that water had been used to fight a plutonium fire. Despite attendant criticality dangers, the use of water was successful in controlling the fire.

The interiors of the two extremely large, high-bay buildings were grossly contaminated. An extensive, long-term cleanup effort was necessary for decontamination. Limited production was restarted about six months later in a temporary production line constructed in an adjacent building.

As damaging as the fire was, the water use prevented breaching of the outer walls and ceiling of 776 and 777, thus preventing a major release of plutonium to the environment. The small amount of plutonium released—almost entirely contained on plant site—was about 0.0002 curies. Slightly contaminated external areas were subsequently cleaned up.

Fortunately, the fire caused no direct deaths. However, one fireman received significant plutonium lung burdens, and other firemen and personnel incurred smaller radiation inhalations and exposures while fighting the fire and later cleaning up heavily contaminated areas.

Immediately prior to the fire, personnel levels were significantly cut with no real decrease in work load or production demands. Strict attention to plutonium chip handling no longer seemed to have been a top priority.

The many lessons learned from this 1969 fire include the following:

- Plutonium pyrophoricity is unpredictable as to when it may occur.
- Combustible materials such as Benelex and Plexiglas should be kept to a minimum in process buildings.
- Uncleaned and uncanned briquettes cannot be left unprotected and unattended on off-shifts.
- Buildings 776-777 were essentially one large room with interconnected glovebox trains with basically no fire breaks or fire walls. This setup allowed for rapid, large- area spread of fire and radioactive contamination.

These lessons learned from the 1969 fire led to a number of safety improvements including the following equipment modifications and procedural revisions prior to the decommissioning of the plant:

- A central, computerized alarm system has been installed.
- A sprinkler/water system has been put in place.
- Gloveboxes with inert atmospheres, heat detectors, and minimal Benelex and Plexiglas shielding are used.
- Water-filled double walls have been constructed.
- Firewater dams on doors are in place.
- Removal of flammable material from gloveboxes is done regularly.
- Briquettes are stored in metal containers with tight lids.
- Containers are placed on metal racks with heat detectors.
- Canning of briquettes is done in an inert atmosphere or vacuum for unattended (overnight or longer) storage.

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Vendor information: For air sensitive reagents see:

http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al134.pdf

For pyrophoric reagents see:

http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al164.pdf

Video: https://www.youtube.com/watch?v=21iC4YEgOAs

Appendix A - Materials Subject to Spontaneous Heating

Materials subject to spontaneous heating (From NFPA Fire Protection Handbook, 20th Edition).

Name	Tendency of Spontaneous Heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Alfalfa meal	High	Bags, bulk	Avoid moisture extremes; tight cars for transportation are essential.	Many fires attributed to spontaneous heating probably caused by sparks, burning embers, or particles of hot metal picked up by the meal during processing. Test fires caused in this manner have smoldered for 72 hours before becoming noticeable.
Burlap bags "used"	Possible	Bales	Keep cool and dry.	Tendency to heat is dependent on previous use of bags. If oily would be dangerous.
Castor oil	Very slight	Metal barrels, metal cans in wooden boxes	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Possible heating of saturated fabrics in badly ventilated piles.
Charcoal	High	Bulk, bags	Keep dry; supply ventilation.	Hardwood charcoal must be carefully prepared and aged. Avoid wetting and subsequent drying.
Coal, bituminous	Moderate	Bulk	Store in small piles; avoid high temperatures.	Tendency to heat depends upon origin and nature of coals. Highly volatile coals are particularly liable to heat.
Cocoa bean shell tankage	Moderate	Burlap bags, bulk	Extreme caution must be observed to maintain safe moisture limits.	This material is very hygroscopic and is liable to heating if moisture content is excessive. Precaution should be observed to maintain dry storage, etc.
Coconut oil	Very slight	Drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Only dangerous if fabrics, etc., are impregnated.
Cod liver oil	High	Drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated organic materials are extremely dangerous.
Colors in oil	High	Drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	May be very dangerous if fabrics, etc., are impregnated.
Copra	Slight	Bulk	Keep cool and dry.	Heating possible if wet and hot.

Name	Tendency of Spontaneous Heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Corn-meal feeds	High	Burlap bags, paper bags, bulk	Material should be processed carefully to maintain safe moisture content and to cure before storage.	Usually contains an appreciable quantity of oil, which has rather severe tendency to heat.
Corn oil	Moderate	Barrels, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Dangerous heating of meals, etc., unlikely unless stored in large piles while hot.
Cottonseed	Low	Bags, bulk	Keep cool and dry.	Heating possible if piled wet and hot.
Cottonseed oil	Moderate	Barrels, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	May cause heating of saturated material in badly ventilated piles.
Distillers' dried grains with oil content (Brewers' grains)	Moderate	Bulk	Maintain moisture 7 to 10%; cool below 100°F (38°C) before storage.	Very dangerous if moisture content is 5% or lower.
-no oil content	Moderate	Bulk	Maintain moisture 7 to 10%; cool below 100°F (38°C) before storage.	Very dangerous if moisture content is 5% or lower.
Feeds, various	Moderate	Bulk, bags	Avoid extremely low or high moisture content.	Ground feeds must be carefully processed. Avoid loading or storing unless cooled.
Fertilizers organic, inorganic, combination of both mixed	Moderate	Bulk, bags	Avoid extremely low or high moisture content.	Organic fertilizers containing nitrates must be carefully prepared to avoid combinations that might initiate heating.
Fertilizers synthetic, containing nitrates and organic matter	Moderate	Bulk, bags	Avoid free acid in preparation.	Ensure ventilation in curing process by small piles or artificial drafts. If stored or loaded in bags, provide ventilation space between bags.
Fish meal	High	Bags, bulk	Keep moisture 6 to 12% Avoid exposure to heat.	Dangerous if over dried or packaged over 100°F (38°C).
Fish oil	High	Barrels, drums, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated porous or fibrous materials are extremely dangerous. Tendency of various fish oils to heat varies with origin.
Fish scrap	High	Bulk, bags	Avoid moisture extremes.	Scrap loaded or stored before cooling is extremely liable to heat.

Name	Tendency of Spontaneous Heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Foam rubber in consumer products	Moderate		Where possible remove foam rubber pads, etc., from garments to be dried in dryers or over heaters. If garments containing foam rubber parts have been artificially dried, they should be thoroughly cooled before being piled, bundled, or put away. Keep heating pads, hair dryers, other heat sources from contact with foam rubber pillows, etc.	Foam rubber may continue to heat spontaneously after being subjected to forced drying as in home or commercial dryers and after contact with heating pads and other heat sources. Natural drying does not cause spontaneous heating.
Grain (various kinds)	Very slight	Bulk, bags	Avoid moisture extremes.	Ground grains may heat if wet and warm.
Hay	Moderate	Bulk, bales	Keep dry and cool.	Wet or improperly cured hay is almost certain to heat in hot weather. Baled hay seldom heats dangerously.
Hides	Very slight	Bales	Keep dry and cool.	Bacteria in untreated hides may initiate heating.
Iron pyrites	Moderate	Bulk	Avoid large piles; keep dry and cool.	Moisture accelerates oxidation of finely divided pyrites.
Istle	Very slight	Bulk, bales	Keep cool and dry.	Heating possible in wet material; unlikely under ordinary conditions. Partially burned or charred fiber is dangerous.
Jute	Very slight	Bulk	Keep cool and dry.	Avoid storing or loading in hot wet piles. Partially burned or charred material is dangerous.
Lamp black	Very slight	Wooden cases	Keep cool and dry.	Fires most likely to result from sparks or included embers, etc., rather than spontaneous heating.
Lanolin	Negligible	Glass, cans, metal drums, barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Heating possible on contaminated fibrous matter.
Lard oil	Slight	Wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Dangerous on fibrous combustible substances.
Lime, unslaked (calcium oxide, pebble lime, Quicklime)	Moderate	Paper bags, wooden barrels, bulk	Keep dry; avoid hot loading.	Wetted lime may heat sufficiently to ignite wood containers, etc.
Linseed	Very slight	Bulk	Keep cool and dry.	Tendency to heat dependent on moisture and oil content.

Name	Tendency of Spontaneous Heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Linseed oil	High	Tank cars, drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Rags or fabrics impregnated with this oil are extremely dangerous. Avoid piles, etc. Store in closed containers, preferably metal.
Manure	Moderate	Bulk	Avoid extremes of low or high moisture contents; ventilate the piles	Avoid storing or loading uncooled manures.
Menhaden oil	Moderate to high	Barrels, drums, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials	Dangerous on fibrous product.
Metal powders[2]	Moderate	Drums, etc.	Keep in closed containers.	Moisture accelerates oxidation of most metal powders.
Metal turnings[2]	Practically none	Bulk	Not likely to heat spontaneously.	Avoid exposure to sparks.
Mineral wool	None	Pasteboard boxes, paper bags	Noncombustible; if loaded hot may ignite containers and other combustible surroundings.	This material is mentioned in this table only because of general impression that it heats spontaneously.
Mustard oil, black	Low	Barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials	Avoid contamination of fibrous combustible materials.
Oiled clothing	High	Fiber boxes	Dry thoroughly before packaging.	Dangerous if material is stored in piles without ventilation.
Oiled fabrics	High	Rolls	Keep ventilated; dry thoroughly before packing	Improperly dried fabrics extremely dangerous. Comparatively tight rolls are safe.
Oiled rags	High	Bales	Avoid storing in bulk in open.	Dangerous if wet with drying oil.
Oiled silk	High	Fiber boxes, rolls	Supply sufficient ventilation.	Improperly dried material is dangerous in form of piece goods. Rolls relatively safe.
Oleic acid	Very slight	Glass bottles, wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated.
Oleo oil	Very slight	Wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	May heat on impregnated fibrous combustible matter.

[2]Refers to iron, steel, brass, aluminum and other common metals. Metals known to heat spontaneously are covered in a later section.

Name	Tendency of Spontaneous Heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Olive oil	Moderate to low	Tank, drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Paint containing drying oil	Moderate	Drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Fabrics, rags, etc., impregnated with paints that contain drying oils and driers are extremely dangerous. Store in closed containers, preferably metal.
Paint scrapings	Moderate	Barrels, drums	Avoid large unventilated piles.	Tendency to heat depends on state of dryness of the scrapings.
Palm oil	Low	Wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Peanut oil	Low	Wooden barrels, tin cans	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Peanuts, "Red Skin"	High	Paper bags, cans, fiber board boxes, burlap bags	Avoid badly ventilated storage.	This is the part of peanut between outer shell and peanut itself. Provide well-ventilated storage.
Peanuts, shelled	Very slight or Negligible	Paper bags, cans, fiber board boxes, burlap bags	Keep cool and dry.	Avoid contamination of rags, etc., with oil.
Perilla oil	Moderate to high	Tin cans, barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Pine oil	Moderate	Galls, drums	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Powdered eggs	Very slight	Wooden barrels	Avoid conditions that promote bacterial growth; inhibit against decay; keep cool.	Possible heating of decaying powder in storage.
Powdered milk	Very slight	Wooden and fiber boxes, metal cans	Avoid conditions that promote bacterial growth; inhibit against decay; keep cool.	Possible heating by decay or fermentation.
Rags	Variable	Bales	Avoid contamination with drying oils; avoid charring; keep cool and dry.	Tendency depends on previous use of rags. Partially burned or charred rags are dangerous.
Red oil	Moderate	Glass bottles, wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated porous or fibrous materials are extremely dangerous. Tendency varies with origin of oil.

Name	Tendency of Spontaneous Heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Roofing felts and papers	Moderate	Rolls, bales, crates	Avoid overdrying the material; supply ventilation.	Felts, etc., should have controlled moisture content. Packaging or rolling uncooled felts is dangerous.
Sawdust	Possible	Bulk	Avoid contact with drying oils; avoid hot, humid storage.	Partially burned or charred sawdust may be dangerous.
Scrap film (nitrate)	Very slight	Drums and lined boxes	Film must be properly stabilized against decomposition.	Nitrocellulose film ignites at low temperature. External ignition more likely than spontaneous heating. Avoid exposure to sparks, etc.
Scrap leather	Very slight	Bales, bulk	Avoid contamination with drying oils.	Oil-treated leather scraps may heat.
Scrap rubber or buffings	Moderate	Bulk, drums	Buffings of high rubber content should be shipped and stored in tight containers.	Sheets, slabs, etc., are comparatively safe unless loaded or stored before cooling thoroughly.
Sisal	Very slight	Bulk bales	Keep cool and dry.	Partially burned or charred material is particularly liable to ignite spontaneously.
Soybean oil	Moderate	Tin cans, barrels, tank cars	Avoid contact with rags, cotton, or fibrous materials.	Impregnated fibrous materials may heat unless well ventilated.
Sperm oil—see whale oil				
Tankage	Variable	Bulk	Avoid extremes of moisture contents; avoid loading or storing while hot.	Very dry or moist tankages often heat. Tendency more pronounced if loaded or stored before cooling.
Tung nut meals	High	Paper bags, bulk	Material must be very carefully processed and cooled thoroughly before storage.	These meals contain residual oil which has high tendency to heat. Material also susceptible to heating if over-dried.
Tung oil	Moderate	Tin cans, barrels, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Turpentine	Low	Tin, glass, barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Has some tendency to heat but less so than the drying oils. Chemically active with chlorine compounds and may cause fire.
Varnished fabrics	High	Boxes	Process carefully; keep cool and ventilated.	Thoroughly dried varnished fabrics are comparatively safe.
Wallboard	Slight	Wrapped bundles, pasteboard boxes	Maintain safe moisture content; cool thoroughly before storage.	This material is entirely safe from spontaneous heating if properly processed.
Waste paper	Moderate	Bales	Keep dry and ventilated.	Wet paper occasionally heats in storage in warm locations.

Name	Tendency of Spontaneous Heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Whale oil	Moderate	Barrels and tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Wool wastes	Moderate	Bulk, bales, etc.	Keep cool and ventilated or store in closed containers; avoid high moisture.	Most wool wastes contain oil, etc., from the weaving and spinning and are liable to heat in storage. Wet wool wastes are very liable to spontaneous heating and possible ignition.

Appendix B – Pyrophoric and Combustible Elements and Compounds Commonly Found Within the DOE Complex

Element/Compound	Formula	Specific Gravity	Melting Point (°C)	Boiling Point (°C)	Solubility	LFL/ UFL (°C)	Flash Point (°C)	Autoignition Temp (°C)	State	Preferred Extinguishing Agent/others in hierarchy
					Cold H_20					
Active Raney Metal Catalyst (Raney-Nickel)	AlNi	8.9[4]	1455[4]	2730[4]	insoluble[4]	ND	ND	87[4]	l	**Preferred:** Water spray, alcohol-resistant foam, CO2 or dry chemical[4]
Aluminum	Al	2.7	660	2452[10]	insoluble	ND	ND	ND	s	**Preferred:** NaCl based agent, dry flux, dry sand NaCl, argon, or allow to burn itself out by forming a ring around the fire with an approved extinguishing agent **Other Effective Agents:** Carbon microspheres or dry soda ash **DO NOT USE:** WATER, FOAM, GRAPHITE BASED AGENTS, LiCl, CO_2, NITROGEN, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS
Aluminum Hydride	AlH_3	1.477	150	ND	Reactive	ND	ND	ND	s	**Preferred:** Class D or other metal extinguishing agent **DO NOT USE:** WATER
Aluminum Silicon Powder	AlSi	1.1[3]	577[3]	ND	insoluble[3]	40 mg/L[3]	ND	650[3]	s	**Preferred:** Gentle surface application of Class D extinguishing agent or dry, inert granular material (e.g. sand) to cover and ring the burning powder. Avoid mixing the extinguishing agent with the burning powder. Do not disturb the powder until completely cool. If possible, isolate burning powder

Element/Compound	Formula	Specific Gravity	Melting Point (°C)	Boiling Point (°C)	Solubility	LFL/ UFL (°C)	Flash Point (°C)	Autoignition Temp (°C)	State	Preferred Extinguishing Agent/others in hierarchy
					Cold H_20					
										DO NOT USE: WATER, FOAM, HALOGENATED AGENTS, OR ABC DRY CHEMICAL EXTINGUISHERS[3]
Arsine	AsH_3	2.69[9]	-116[9]	-62[9]	20cc/ 100cc H_20[9]	4.5/78[9]	-62[9]	285[9]	g	**Preferred:** Stop the flow of gas **Other Effective Agents:** CO_2 **NO NOT USE:** WATER
Barium, Finely Divided	Ba	3.5[9]	725[10]	1140[10]	Reactive[9]	ND	ND	ND	s	**Preferred:** dry chemical/dolomite (powdered limestone) or NaCl **DO NOT USE:** WATER, FOAM, CO_2, HALOGENATED AGENTS, OR HALOGENATED AGENTS[9]
Calcium	Ca	1.55	824[10]	1440[10]	decompose s	ND	ND	ND	s	**Preferred:** NaCl based agent, dry flux, dry sand, NaCl, argon, or allow to burn itself out **Other Effective Agents:** Carbon Microspheres, dry soda ash, or boron triflouride **DO NOT USE:** WATER, FOAM, GRAPHITE BASED AGENTS, COPPER POWDER, LiCl, CO_2, NITROGEN, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS
Cerium (powder)	Ce	6.67	795	3257	decompose s	ND	ND	ND	s	**Preferred:** Class D or other metal extinguishing agent **DO NOT USE:** WATER
Diborane	B_2H_6	0.21[1]	-156[1]	-92.5[1]	Insoluble[1]	0.9/98	-148.15	51.85	g	**Preferred:** Stop the flow of gas

Element/Compound	Formula	Specific Gravity	Melting Point (°C)	Boiling Point (°C)	Solubility	LFL/ UFL (°C)	Flash Point (°C)	Autoignition Temp (°C)	State	Preferred Extinguishing Agent/others in hierarchy
					Cold H_20					
										Other Effective Agents: WATER **DO NOT USE:** HALOGENATED AGENTS
Hafnium	Hf	13.31[9]	2223[10]	5399[10]	insoluble[9]	ND	ND	ND	s	**Preferred:** NaCl based agent, argon, or helium. **Other Effective Agents:** Allow to burn itself out **DO NOT USE**: WATER, FOAM, CO2, OR HALOGENATED AGENTS
Hydrazine	$N2H_4$	1.011 to 1.4	1.4	113.5	infinity	ND	38[1]	23[1]	l	**Preferred:** SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. **DO NOT USE**: WATER JET
Iron	Fe	7.86	1535	3000	insoluble	ND	ND	ND	s	**Preferred:** SMALL FIRE: Use dry chemical powder. LARGE FIRE: Carefully use water spray, fog or foam. **Other Effective Agents:** Carbon microspheres, NaCl based agents, dry sand, argon, or nitrogen **DO NOT USE:** WATER JET, GRAPHITE BASED AGENTS, COPPER POWDER, DRY FLUX, LiCl, DRY SODA ASH, NaCl, CO_2, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENT.
Lithium	Li	0.53	186	1336[10]	decomposes	ND	ND	ND	s	**Preferred:** Graphite based agent or copper powder **Other Effective Agents:** Carbon microspheres, dry flux, dry sand, LiCl,

Element/Compound	Formula	Specific Gravity	Melting Point (°C)	Boiling Point (°C)	Solubility	LFL/ UFL (°C)	Flash Point (°C)	Autoignition Temp (°C)	State	Preferred Extinguishing Agent/others in hierarchy
					Cold H_20					
										dry soda ash, NaCl, argon, or helium. (AFF Foam has been shown to be effective if used in the incipient stage) **DO NOT USE**: WATER, CO2, NaCl BASED AGENTS, NITROGEN, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS
Magnesium	Mg	1.74	650[10]	1110	insoluble	ND	ND	473[1]	s	**Preferred:** NaCl based agent, dry flux, dry sand, NaCl, argon, or allow to burn itself out. **Other Effective Agents:** Carbon Microspheres, graphite based agents, dry soda ash, or boron triflouride **DO NOT USE:** WATER, FOAM, COPPER POWDER, LiCl, CO_2, NITROGEN, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS
Neodymium Iron Boron Alloy Powder	NdFeB	7.4	1832	ND	insoluble	ND	ND	ND	s	**Preferred:** Dry chemicals or dry sand
Nickel-Aluminum Alloy, Powder	Ni-Al	7.4[7]	ND	1350[7]	insoluble[7]	ND	ND	760[7]	s	**Preferred:** Dry sand, dry dolomite, or dry graphite powder or other dry chemical extinguishing agent formulated for metal fires **DO NOT USE:** WATER OR HALOGENATED AGENTS
Phosphine	Ph_3	0.75	-132.5	-85	26cc/ 100cc H_20	1/98	ND	100[1]	g	**Preferred:** Stop the flow of gas **DO NOT USE:** HALOGENATED AGENTS
White Phosphorus	P4	1.83[6]	44[6]	ND	soluble[6]	ND	ND	30[6]	s	**Preferred:** Foam, water, wet sand or earth, argon, or helium

Element/Compound	Formula	Specific Gravity	Melting Point (°C)	Boiling Point (°C)	Solubility	LFL/ UFL (°C)	Flash Point (°C)	Autoignition Temp (°C)	State	Preferred Extinguishing Agent/others in hierarchy
					Cold H_20					
										DO NOT USE: ALKALINE BASED AGENTS[6]
Plutonium	Pu	19.86	640	3315[10]	insoluble	ND	ND	Self-Heating	s	**Preferred:** MgO[11] **Other Effective Agents:** Dry sand, graphite powder, NaCl based agent, PuO_2, argon, water can be used if adequate ventilation is present for hydrogen production and there is no criticality concern[11] **DO NOT USE:** HALOGENATED AGENTS[11]
Potassium	K	0.86	62[10]	760	reactive	ND	ND	ND	s	**Preferred:** NaCl based agent **DO NOT USE:** WATER, FOAM, CO_2, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS[2]
Praseodymium (Powder)	Pr	6.77[8]	935[8]	3130[8]	decomposes[8]	ND	ND	ND	s	**Preferred:** Dry chemical, Class D extinguisher **DO NOT USE:** WATER[8]
Rubidium	Rb	1.53	38.5	700	insoluble	ND	ND	Self-Heating	s	**Preferred:** Class D or other metal extinguishing agent **DO NOT USE:** WATER, FOAM, OR CO_2
Silane	SiH_4	0.68	-185	-112	insoluble	0.8/98	ND	Any[1]	g	**Preferred:** Stop the flow of gas **DO NOT USE:** HALOGENATED AGENTS
Sodium	Na	0.97	98[10]	880	decomposes, forms NaOH	ND	ND	ND	s	**Preferred:** NaCl based agent, graphite based agent, copper powder, argon, nitrogen, Class D or other metal extinguishing agent **Other Effective Agents:** include

Element/Compound	Formula	Specific Gravity	Melting Point (°C)	Boiling Point (°C)	Solubility Cold H_20	LFL/ UFL (°C)	Flash Point (°C)	Autoignition Temp (°C)	State	Preferred Extinguishing Agent/others in hierarchy
										carbon microspheres, dry sand, dry soda ash, dry LiCl, or dry NaCl **DO NOT USE:** WATER, FOAM, CO_2, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS[2]
Sodium-Potassium	NaK	0.86	-12.6	785	Reactive	ND	ND	120	l	**Preferred:** NaCl based agent, graphite based agent, copper powder, argon, nitrogen, Class D or other metal extinguishing agent **Other Effective Agents:** Include carbon microspheres, dry sand, dry soda ash, dry LiCl, or dry NaCl **DO NOT USE:** WATER, FOAM, CO2, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS
Strontium	Sr	2.6	800	1150	decomposes into $Sr(OH)_2$	ND	ND	ND	s	**Preferred:** NaCl based agent, dry flux, dry sand, NaCl, argon, or allow to burn itself out **Other Effective Agents:** Carbon Microspheres, dry soda ash, or boron triflouride **DO NOT USE:** WATER, FOAM, GRAPHITE BASED AGENTS, COPPER POWDER, LiCl, CO_2, NITROGEN, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS
Thorium	Th	11.2	1845	4500[10]	insoluble	ND	ND	ND	s	**Preferred:** NaCl based agent, dry MgO, or dry sand **Other Effective Agents:** Water can be used if adequate ventilation is

Element/Compound	Formula	Specific Gravity	Melting Point (°C)	Boiling Point (°C)	Solubility	LFL/ UFL (°C)	Flash Point (°C)	Autoignition Temp (°C)	State	Preferred Extinguishing Agent/others in hierarchy
					Cold H_20					
										present for hydrogen production and there is no criticality concern[2]
Titanium	Ti	4.5	1727[10]	3260[10]	insoluble	ND	ND	1200 (Solid)/ 250 (Powder)[1]	s	**Preferred:** NaCl based agent, dry sand, NaCl, LiCl, argon, or allow to burn itself out **Other Effective Agents:** Carbon Microspheres, graphite, or dry soda ash **DO NOT USE:** WATER, FOAM, GRAPHITE BASED AGENTS, DRY FLUX, COPPER POWDER, CO_2, NITROGEN, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS
Uranium	U	18.95	1132[10]	3815[10]	insoluble	ND	ND	100	s	**Preferred:** MgO **Other Effective Agents:** Dry sand, graphite powder, NaCl based agent, PuO_2, argon, water can be used if adequate ventilation is present for hydrogen production and there is no criticality concern. **DO NOT USE:** HALOGENATED AGENTS[2]
Zinc	Zn	7.14	419	907	insoluble	ND	ND	Self-Heating	s	**Preferred:** NaCl based agent, dry flux, dry sand, NaCl, argon, or allow to burn itself out **Other Effective Agents:** Carbon Microspheres, dry soda ash, or boron triflouride **DO NOT USE:** WATER, FOAM,

Element/Compound	Formula	Specific Gravity	Melting Point (°C)	Boiling Point (°C)	Solubility	LFL/ UFL (°C)	Flash Point (°C)	Autoignition Temp (°C)	State	Preferred Extinguishing Agent/others in hierarchy
					Cold H_20					
										GRAPHITE BASED AGENTS, COPPER POWDER, LiCl, CO_2, NITROGEN, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS
Zirconium	Zr	6.4	1830[10]	3577[10]	insoluble	ND	ND	Self-Heating	s	**Preferred:** NaCl based agent, dry sand, NaCl, LiCl, argon, helium, or allow to burn itself out **Other Effective Agents:** Carbon Microspheres or dry soda ash **DO NOT USE:** WATER, FOAM, GRAPHITE BASED AGENTS, DRY FLUX, COPPER POWDER, CO_2, NITROGEN, HALOGENATED AGENTS, OR HYDROCARBON CLEAN AGENTS

ND stands for No Data

* The above table contains elements and compounds most commonly found within the DOE Complex and should not be considered an unabridged list. For additional materials/information, please refer to the most current edition of NFPA 484 and the applicable Safety Data Sheet.

** Unless otherwise noted, the above material properties are from Perry's Chemical Engineers Handbook 8th Ed.

[1] The U.S. National Library of Medicine, WISER (2014)
[2] The Los Alamos National Laboratory Fire Department Training Manual, 2013
[3] ALCOA Inc., MSDS ID# 126, Aluminum-Silicon, 2007
[4] SIGMA-ALDRICH, MSDS for Raney-Nickle, 2013
[5] ESPI Metals, MSDS for Cerium, 2005
[6] OXY Glenn Springs Holding, Inc., MSDS ID# M7588, White Phosphorus, 2008
[7] AMETEK Specialty Metal Products Division, MSDS ID# 82, Nickle Aluminum Alloy Powder, 2006
[8] ESPI Metals, MSDS for Praseodymium, 2005
[9] HMEx Assistant V6.2.0
[10] National Fire Protection Association, NFPA 484 (2015)
[11] Burning and Extinguishing Characteristics of Plutonium Metal Fires, R.E. Felt, 1967